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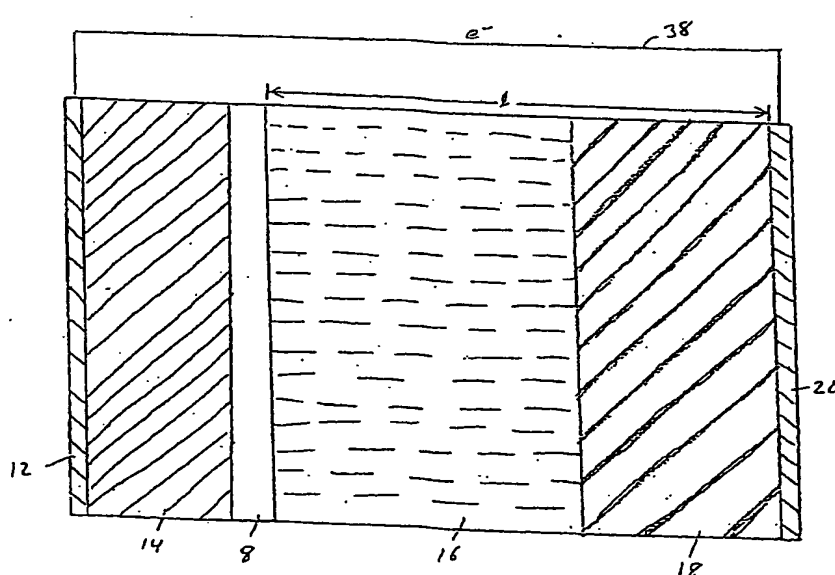
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(54) Title: **LIQUID ELECTROLYTE LITHIUM-SULFUR BATTERIES**



(57) Abstract: A high performance lithium-sulfur battery cell (10) includes the following features: (a) a negative electrode (14) including a metal or an ion of the metal; (b) a positive electrode (18) comprising an electronically conductive material; and (c) a liquid catholyte (16) including a solvent and a dissolved electrochemically active material comprising sulfur in the form of a sulfide of the negative electrode metal or a polysulfide of the metal. Such battery cells are characterized by an energy density, calculated based upon a laminate weight, of at least 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². Cells meeting these criteria often find use as primary cells.

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LIQUID ELECTROLYTE LITHIUM-SULFUR BATTERIES

BACKGROUND OF THE INVENTION

This invention relates to metal-sulfur batteries (e.g., lithium-sulfur batteries).

5 The rapid proliferation of portable electronic devices in the international marketplace has led to a corresponding increase in the demand for advanced secondary batteries (i.e., rechargeable batteries). The miniaturization of such devices as, for example, cellular phones, laptop computers, etc., has naturally fueled the desire for rechargeable batteries having high specific energies (light weight). At the same
10 time, mounting concerns regarding the environmental impact of throwaway technologies, has caused a discernible shift away from primary batteries and towards rechargeable systems.

 In addition, heightened awareness concerning toxic waste has motivated, in part, efforts to replace toxic cadmium electrodes in nickel/cadmium batteries with the
15 more benign hydrogen storage electrodes in nickel/metal hydride cells. For the above reasons, there is a strong market potential for environmentally benign secondary battery technologies.

 Secondary batteries are in widespread use in modern society, particularly in applications where large amounts of energy are not required. However, it is desirable
20 to use batteries in applications requiring considerable power, and much effort has been expended in developing batteries suitable for high specific energy, medium power applications, such as, for electric vehicles and load leveling. Of course, such batteries would also be suitable for use in lower power applications such as cameras or portable recording devices. Primary batteries having specific energies and high power
25 densities also find use in many applications.

 Among the factors leading to the successful development of high specific energy batteries is the fundamental need for high cell voltage and low equivalent weight electrode materials. Electrode materials must also fulfill the basic electrochemical requirements of sufficient electronic and ionic conductivity, high
30 reversibility of the oxidation/reduction reaction, as well as excellent thermal and chemical stability within the temperature range for a particular application. Importantly, the electrode materials must be reasonably inexpensive, widely available, non-explosive, non-toxic, and easy to process.

Thus, a smaller, lighter, cheaper, non-toxic battery is sought for the next generation of batteries. The low equivalent weight of lithium renders it attractive as a battery electrode component for improving weight ratios. Lithium also provides greater energy per volume than do the traditional battery standards, nickel and cadmium.

The low equivalent weight and low cost of sulfur and its nontoxicity renders it also an attractive candidate battery component. Successful lithium/organosulfur battery cells are known. (See, De Jonghe et al., U.S. patent Nos. 4,833,048 and 4,917,974; and Visco et al., U.S. Patent No. 5,162,175.)

Recent developments in ambient-temperature sulfur electrode technology may provide commercially viable rechargeable lithium-sulfur batteries. Chu and colleagues are largely responsible for these developments which are described in the above-referenced U.S. Patent Nos. 5,582,623 and 5,523,179 (issued to Chu). These developments allow electrochemical utilization of elemental sulfur at levels of 50% and higher over multiple cycles. Because sulfur has a theoretical maximum capacity of 1675 mAh/g (assuming all sulfur atoms in an electrode are fully reduced during discharge), the utilization of sulfur in lithium-sulfur cells as described in the above Chu patents typically exceeds 800 milliamp-hours per gram (mAh/g) of sulfur. Chu's initial work focused on solid and gel-state batteries in which a solid or gel-state ionic conductor was immobilized with the sulfur in an electrode.

Prior to Chu's work, rechargeable ambient-temperature lithium-sulfur batteries were not considered commercially viable. The limited research that was conducted in the field almost universally employed liquid electrolytes which served not only as ionic transport media between the anode and cathode, but also as ionic conductors within the sulfur electrode. Without exception, these electrodes suffered from poor utilization of the sulfur electrode over repeated cycling. For example, one of the best reported rechargeable lithium-sulfur liquid electrolyte batteries cycled 120 times, but had a maximum sulfur utilization of only 5%. See Rauh, R.D., Pearson, G.F. and Brummer, S.B., "Rechargeability Studies of Ambient Temperature Lithium/Sulfur Batteries", 12TH IECEC, 283-287 (1977). Other rechargeable systems had higher sulfur utilizations, but unacceptably low cycle lives. For example, one group reports a maximum sulfur utilization of about 45%, but their cell was dead by 50 cycles and, during cycling, had a utilization of only about 25%. See Peled, E., Gorenstein, A., Segal, M., Sternberg, Y., "Rechargeable Lithium-Sulfur Battery (Extended Abstract)", J. Power Sources, 26, 269-271, (1989). Because of their poor cycling performance, the vast majority of prior lithium-battery systems were at best deemed suitable only as

primary batteries. And even then, they were only functional at very low current densities. In addition, some researchers have concluded that liquid electrolyte/sulfur cells will be intrinsic limited to poor performance. See Coleman, J.R. and Bates, M.W., "The Sulfur Electrode", 289-302 (1968)

5 Other references to lithium-sulfur battery systems in liquid formats include the following: Yamin et al., "Lithium Sulfur Battery," J. Electrochem. Soc., 135(5): 1045 (May 1988); Yamin and Peled, "Electrochemistry of a Nonaqueous Lithium/Sulfur Cell," J. Power Sources, 9: 281 (1983); Peled et al., "Lithium-Sulfur Battery: Evaluation of Dioxolane-Based Electrolytes," J. Electrochem. Soc., 136(6): 1621
10 (June 1989); Bennett et al., U.S. Patent No. 4,469,761; Farrington and Roth, U.S. Patent No. 3,953,231; Nole and Moss, U.S. Patent No. 3,532,543; Lauck, H., U.S. Patent Nos. 3,915,743 and 3,907,591; Societe des Accumulateurs Fixes et de Traction, "Lithium-sulfur battery," Chem. Abstracts, 66: Abstract No. 111055d at page 10360 (1967); and Lauck, H. "Electric storage battery with negative lithium electrode and
15 positive sulfur electrode," Chem. Abstracts, 80: Abstract No. 9855 at pages 466-467 (1974).).

It now appears that the poor performance of the prior art lithium-sulfur cells resulted from various design flaws. For example, many cells employed large
20 reservoirs of liquid electrolyte in which sulfide and polysulfide discharge products dissolved, diffused away from the positive electrode, and became unavailable for further electrochemical reaction, thereby reducing the cell's capacity. In addition, it is likely that the prior art cells were operated under conditions in which their discharge products were irreversibly precipitated out of solution, thereby reducing capacity.

Still further, poor performance of the prior art cells may result from failure to
25 optimize the catholyte composition in conjunction with the cathode structure. Many prior art cathodes made use of traditional carbon structures including high surface area carbon and binder pressed into expanded metal. There are many disadvantages to such a design. First the pore structure of such cathodes limits the transport rate of dissolved sulfur species which leads to premature precipitation of sulfide discharge
30 products that leads to clogging of the positive electrode and then to cell polarization. Second, such cathodes may not have had an open pore structure, so that a significant part of the sulfur capacity is retained outside of the active area of the electrode.

What is needed therefore is a safe liquid electrolyte metal-sulfur battery system optimized for the chemical and electrochemical features of the sulfur rechargeable
35 electrode.

SUMMARY OF THE INVENTION

The present invention provides high performance thin film lithium-sulfur battery cells having liquid electrolytes. The cells preferably include the following features: (a) a negative electrode including a metal or an ion of the metal; (b) a positive electrode comprising an electronically conductive material; and (c) a liquid catholyte including a solvent and dissolved electrochemically active material comprising sulfur in the form of at least one of a sulfide of the metal and a polysulfide of the metal. Such battery cells are characterized by an energy density, calculated based upon a laminate weight, of at least about 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². Cells meeting these criteria often find use as primary cells.

In a preferred embodiment, the liquid catholyte has a sulfur concentration of at least about 6 M, more preferably at least about 7 M, and most preferably at least about 10 M. Preferably, the electrolyte solvent includes an ether such as dimethoxyethane. The electrolyte may include a cosolvent such as dioxolane. The electronically conductive material in the positive electrode may include at least one of carbon and an electronically conductive polymer. To ensure good utilization, the conductive material preferably comprises an interconnected matrix. In a primary cell, the positive electrode may be made relatively thick; e.g., having an average thickness of at least about 40 micrometers (not including the current collector).

Often the negative electrode is an alkali metal electrode such as a lithium metal electrode. Preferably, the negative electrode includes a protective layer that is conductive to ions of the metal and protects the electrode from attack by the electrolyte or sulfur.

Another aspect of the invention provides a rechargeable battery cell that may be characterized by the following features: (a) a negative electrode including a metal or an ion of the metal; (b) a positive electrode comprising a mixture of an electronically conductive material; and (c) a liquid catholyte including a solvent and dissolved electrochemically active material comprising sulfur in the form of at least one of a sulfide of the metal and a polysulfide of the metal. Such cell is further characterized by at least one of the following criteria: (i) the battery cell attains at least about 10% utilization over at least fifty cycles, and (ii) the battery cell attains at least about 50% utilization over two or more cycles. More stringent criteria include (iii) the battery cell attains at least about 30% utilization over at least 50 cycles or (iv)

the battery cell attains at least about 50% utilization over at least 10 cycles, or (v) the battery cell attains at least about 50% utilization over at least 75 cycles. Concerning discharge rate, the cell preferably discharges at an average current density of at least about 0.5 mA/cm² over at least 50 cycles in criteria (i) and at least 2 cycles in criteria
5 (ii). The positive electrode, negative electrode, and electrolyte preferably meet the criteria set out above for another aspect of the invention.

These and other features of the invention will be further described and exemplified in the drawings and detailed description below.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a lithium/liquid electrolyte/sulfur cell of this invention.

Figure 2 is a process flow diagram of a preferred method for fabricating positive electrodes that may be employed in this invention.

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Figure 3 is a table presenting various slurry compositions employed to fabricate sulfur electrodes for use in cells of this invention.

Figure 4 is a graph showing laminate power density versus laminate energy density for various primary cells constructed in accordance with this invention.

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Figure 5 is a graph showing laminate power density versus laminate energy density for various secondary cells constructed in accordance with this invention.

Figure 6 is a table presenting the results of various experiments conducted in accordance with this invention.

Figure 7 is a graph of end of discharge voltage after each recharge cycle for the cell described in Example 1.

25

Figure 8 is a graph of the percent sulfur utilization after each recharge cycle for the cell described in Example 2.

Figure 9 is a graph of percent sulfur utilization versus cycle number for the cell described in Example 3.

Figure 10 is a graph of the percent sulfur utilization versus number of recharge
30 cycles for the cell described in Example 4.

Figure 11 is a graph of percent sulfur utilization versus number or recharge cycles for the cell described in Example 5.

Figure 12 is a graph of percent sulfur utilization versus number or recharge cycles for the cell described in Example 6.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

INTRODUCTION

This invention provides metal-sulfur batteries having low equivalent weight, high cell voltage and consequently a high specific energy, and operating at high sulfur utilization over many cycles. The batteries are preferably constructed in a thin film format such that the current density does not become diffusion limited. The invention also provides primary metal-sulfur cells having high specific energy.

In one embodiment, the battery cells of this invention include a liquid electrolyte solvent that contains one or more ethers. Preferably, the main electrolyte solvent includes a glyme or related compound. In a particularly preferred embodiment, the electrolyte includes dimethoxyethane (DME) and dioxolane.

The positive electrodes employed in batteries of this invention include a sulfur-based material having a relatively low equivalent weight. The electrodes, which may be composites, include in their theoretically fully charged state sulfur and an electronically conductive material. At some state of discharge, the positive electrode will include one or more of sulfides and polysulfides, which are sulfides and polysulfides of the metal or metals found in the negative electrode. In some embodiments, the fully charged electrode may also include some amount of such sulfides and/or polysulfides.

Sometimes the sulfur-based electroactive material in a positive electrode may be generally referred to as "active sulfur." As used herein, that term refers to electroactive material that is elemental sulfur or discharge products of elemental sulfur that would return to elemental sulfur in a theoretically fully charged state.

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Upon discharge, the sulfur of the positive electrode reacts with the metal of the negative electrode to form the metal sulfides and polysulfides. For example, where M is the metal of the negative electrode, the overall cell reaction can be described as follows:

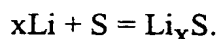


where M is any metal that can function as an active component in a negative electrode in a battery cell in which sulfur is the active component of the positive electrode; x = 0 through x = 2; z = the valence of the metal; and S is sulfur.

M is preferably at least one of an alkali metal, an alkaline earth metal, and a transition metals. M is more preferably selected an alkali metal, and still more preferably lithium or sodium. M is most preferably lithium.

10

In a preferred embodiment of this invention where the negative electrode contains lithium, the overall cell reaction wherein z = 1 can be described as follows:



15 When x = 2, 100% of the theoretical specific energy of the system has been released. If all elemental sulfur in the positive electrode reacts completely (so that all sulfur resides in Li₂S), the sulfur in the electrode is 100% utilized so that all 1675 mAh/g of sulfur is extracted during discharge.

From the above discussion, it should be apparent that upon discharge the positive electrode becomes a combination of sulfur, metal sulfides and polysulfides, and during the discharging process the proportions of those sulfur-containing components will change according to the state of charge. The charge/discharge process in the positive electrode is reversible. Similarly, upon recharging, the percentages of the sulfur-containing ingredient will vary during the process.

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25 The positive electrode is fabricated such that it permits electrons to easily move between the sulfur and the electronically conductive material, and permits ions to move between the electrolyte and the sulfur. Thus, high sulfur utilization is realized after many cycles.

The present invention contemplates cell designs in which (1) all active sulfur is dissolved in electrolyte solution (one phase positive electrode) and (2) cell designs in which the active sulfur is distributed between a solid phase (sometimes precipitated) and a liquid phase. Each design has its advantages. The first design (all

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sulfur is dissolved in the electrolyte) can be operated without producing precipitated active sulfur. Thus, there is less danger of the cell capacity being reduced due to unavailable precipitated electroactive species. The second design has a greater specific energy because the solid phase active sulfur contains a higher density of electroactive material. While the second design does have to contend with precipitated active sulfur and the possibility that electroactive species will be lost, certain design criteria can be employed to mitigate this potential detriment. For example, the cell can be configured or operated under conditions to minimize precipitation.

In a two phase design, the range of sulfur in such electrodes in the theoretically fully charged state is preferably from about 10% to 90% (more preferably 30% to 80%) by weight, excluding electrolyte. The sulfur-based composite electrode is preferably processed such that the component particles are homogeneously distributed, and segregation and/or agglomeration of the component particles is avoided.

A metal-sulfur battery system constructed with the sulfur-based positive electrode of this invention should have at least about 10%, and more preferably at least about 30%, availability of the sulfur, and most preferably at least about 50% availability of sulfur (during a single cycle). This availability corresponds to a minimum of 168 mAh/g (more preferably 504 mAh/g and most preferably 838 mAh/g) of sulfur included in the positive electrode. This is based on the above-mentioned theoretical value of 1675 mAh/gm of sulfur at 100% availability.

BATTERY DESIGN

Suitable batteries may be constructed according to the known art for assembling cell components and cells as desired, and any of the known configurations may be fabricated utilizing the invention. The exact structures will depend primarily upon the intended use of the battery unit. Examples include thin film with porous separator, thin film polymeric laminate, jelly roll (i.e., spirally wound), prismatic, coin cell, etc.

The negative electrode is spaced from the positive sulfur electrode, and both electrodes may be in material contact with an electrolyte separator. Current collectors contact both the positive and negative electrodes in a conventional manner and permit an electrical current to be drawn by an external circuit. In a typical cell, all of the

components will be enclosed in an appropriate casing, for example, plastic, with only the current collectors extending beyond the casing. Thereby, reactive elements, such as sodium or lithium in the negative electrode, as well as other cell elements are protected.

5 Conventional cell designs are known in the art, which may be consulted for details. Examples of sulfur cells employing various design configurations are set forth in the following references which are incorporated herein by reference for all purposes: (1) R.D. Rauh, F.S. Shuker, J.M. Marston and S.B. Brummer, J. Inorg. Nuc. Chem., "Formation of Lithium Polysulfides in Aprotic Media", 39, 1761 (1977);
10 (2) R.D. Rauh, K.M. Abraham, G. F. Pearson, J.K. Suprenant and S.B. Brummer, "A Lithium/Dissolved Sulfur Battery with an Organic Electrolyte," J. Electrochem. Soc., 126, 523 (1979); (3) H. Yamin, A. Gorenshtein, J. Penciner, Y. Sterberg, and E. Peled, "Lithium Sulfur Battery," J. Electrochem. Soc., 135, 1045 (1988); (4) H. Yamin and E. Peled, "Electrochemistry of a Nonaqueous Lithium/Sulfur Cell," J. Power
15 Sources, 9, 281 (1983); and (5) E. Peled, Y. Sterberg, A. Gorenshtein, and Y. Lavi, "Lithium-Sulfur Battery: Evaluation of Dioxolane-Based Electrolyte," J. Electrochem. Soc., 136, 1621 (1989).

Referring now to Figure 1, a cell 10 in accordance with a preferred embodiment of the present invention is shown. Cell 10 includes a negative current
20 collector 12, which is formed of an electronically conductive material. The current collector serves to conduct electrons between a cell terminal (not shown) and a negative electrode 14 (such as lithium) to which current collector 12 is affixed. If negative electrode 14 is made from lithium or other similarly reactive material, it will preferably include a protective layer 8 formed opposite current collector 12. Either
25 negative electrode 14 or protective layer 8 (if present) contacts a liquid electrolyte in an electrolyte region 16.

Region 16 may be delineated by the boundaries of a separator, which prevents electronic contact between the positive and negative electrodes. A positive electrode 18 abuts the side of separator layer 16 opposite negative electrode 14. As electrolyte
30 region 16 is an electronic insulator and ionic conductor, positive electrode 18 is ionically coupled to but electronically insulated from negative electrode 14. Finally, the side of positive electrode 18 opposite electrolyte region 16 is affixed to a positive current collector 20. Current collector 20 provides an electronic connection between a positive cell terminal (not shown) and positive electrode 18.

35 Current collectors 12 and 20, which provide current connections to the positive and negative electrodes, should resist degradation in the electrochemical environment

of the cell and should remain substantially unchanged during discharge and charge. In one embodiment, the current collectors are sheets of conductive material such as aluminum, copper, or stainless steel. The positive electrode may be attached to the current collector by directly forming on the current collector or by pressing a pre-formed electrode onto the current collector. Positive electrode mixtures formed directly onto current collectors preferably have good adhesion. Positive electrode films can also be cast or pressed onto expanded metal sheets. Alternately, metal leads can be attached to the positive electrode by crimp-sealing, metal spraying, sputtering or other techniques known to those skilled in the art. The sulfur-based positive electrode can be pressed together with the electrolyte separator sandwiched between the electrodes. In order to provide good electrical conductivity between the positive electrode and a metal container, an electronically conductive matrix of, for example, carbon or aluminum powders or fibers or metal mesh may be used.

In the case where sulfur is provided entirely as a dissolved species in the electrolyte, positive electrode 18 may primarily include an electronic conductor such as a carbon fiber matrix together with a binder or other additives. In the case where sulfur is provided in both the solid and liquid (dissolved) phases, positive electrode 18 will include some amount of active sulfur in conjunction with the electronic conductor and possibly additives.

The separator may occupy all or some part of electrolyte compartment 16. Preferably, it will be a highly porous/permeable material such as a felt, paper, or microporous plastic film. It should also resist attack by the electrolyte and other cell components under the potentials experienced within the cell. Examples of suitable separators include glass, plastic, ceramic, and porous membranes thereof among other separators known to those in the art. In one specific embodiment, the separator is Celgard 2300 or Celgard 2400 available from Hoechst Celanese of Dallas, Texas.

The separator may also be of the type sometimes referred to as a "polymer" separator membrane having a porous or microporous network for entraining liquid electrolyte. Such separators are described in US Patent No. 3,351,495 assigned to W. R. Grace & Co. and US Patent Nos. 5,460,904, 5,540,741, and 5,607,485 all assigned to Bellcore, for example. These patents are incorporated herein by reference for all purposes.

In a preferred embodiment, the metal-sulfur cell has relatively thick positive and negative electrodes. Such thick format cells are particularly beneficial for use as primary cells, although they are appropriate in some secondary cells as well. The additional material provided in the electrodes provides extra capacity for long life. In

a specific example, the positive electrode of a primary cell has an average thickness of at least about 40 micrometers and the positive electrode of a secondary cell has an average thickness of at most about 8 micrometers. These thicknesses apply to electrodes in which all sulfur is provided by the catholyte and those in which at least some sulfur is provided in the solid phase and localized at the electrode. Generally such thicknesses represent a bare minimum and are appropriate with very high concentration catholytes (e.g., 15 Molar sulfur or possibly even 25 Molar sulfur). In more typical embodiments, the positive electrode thickness will range between about 40 and 130 micrometers for primary cells and between about 8 and 30 micrometers for secondary cells. Note that it may be feasible and appropriate to provide sulfur as a suspension (e.g., a colloid) in the catholyte. Note also that it is generally desirable that the positive electrode have a relatively high porosity, possibly as high as 95% or more. Generally, higher porosity electrodes allow fabrication of cells with higher laminate energy densities because less electronic conductor is required. Of course, an electrode's porosity, capacity, and thickness are linked so that setting two of these parameters fixes the other.

ELECTROCHEMICAL AND CHEMICAL MECHANISMS OF LITHIUM-SULFUR LIQUID ELECTROLYTE BATTERIES

Referring again to Figure 1, lithium-sulfur cell 10 will be described with relevant reaction mechanisms explained. During normal charging, the electrons are extracted from positive electrode 18 and transported over electrical connection 38 to negative electrode 14. The removal of electrons at positive electrode 18 oxidizes the species present in the electrode. In this reaction, lithium ions are liberated from lithium sulfide and/or lithium polysulfide species present in the positive electrode. The species remaining in the positive electrode will have the general formula Li_2S_x , where x has a value of 1 or greater. Over time the charge reaction produces polysulfide species having longer and longer sulfur chains. It is known for example that in a normal charge reaction, the value of x in some polysulfides may be 12 or greater. In addition, some of the polysulfides will be further oxidized to elemental sulfur.

At the negative electrode, lithium ions present in the electrolyte 16 are transported through protective layer 8 and reduced to lithium metal as electrons are moved through electrical conduit 38.

The above electrode reactions proceed in the reverse direction during discharge. That is, the electrochemical reduction of active sulfur pulls electrons to positive electrode 18 through current collector 20 and from line 38. This reduces elemental sulfur, if present, to form various lithium species including lithium polysulfides and lithium sulfide. It also reduces the highly oxidized polysulfides to less oxidized polysulfides and lithium sulfide. Simultaneously, lithium ions are provided from negative electrode 14 through the electrolyte. The lithium ions are generated in conjunction with the flow of electrons from negative electrode 14 to line 38 (via current collector 12).

Generally, the higher molecular weight polysulfides (those with more sulfur atoms) are more highly soluble than their lower molecular weight counterparts. During discharge, these higher molecular weight species go into solution in the electrolyte and migrate throughout the cell. Some of the dissolved species move to the negative lithium metal electrode where they may be chemically reduced to form less-soluble lower molecular weight compounds such as lithium sulfide. Some of this lithium sulfide may beneficially act as a protective layer on the lithium metal electrode. However, lithium sulfide formed in excess of this beneficial amount may precipitate out a solution where it serves no beneficial use in the cell. In fact, this precipitated lithium sulfide (and/or less-soluble lower molecular weight polysulfides) represents lithium and sulfur that is no longer available for immediate participation in electrochemical reactions. Thus, precipitation of these compounds reduces the battery's capacity.

Precipitated sulfide or polysulfide may also form because the local solution concentration of these species exceeds their solubility limits. This occurs when the species are generated faster than they can diffuse away, a condition that exists when the local current density is too great in comparison with the mass transport rate. That is, the solution phase concentration gradient must support a mass flux that is sufficiently high to remove reaction products before they accumulate to their solubility limit. The present invention addresses this problem in at least two ways. First, it provides electrolyte solvents in which the discharge species are highly soluble and highly mobile thereby reducing the likelihood of precipitation. Second, it provides a cathode structure in which the mass flux is sufficiently fast that the local concentration of soluble species does not exceed the solubility limits.

Assuming that some precipitation will occur so that solid phase sulfur, sulfide, and/or polysulfide exist in the cell, it is important that the cell be designed to make these precipitated electroactive species available to electronic and ionic charge

carriers. This allows high utilization of the active sulfur in the cell. To this end, the electronic conductor in the positive electrode should form an interconnected matrix so that there is always a clear current path from the positive current collector to any position in the electronic conductor. The interconnected matrix of the electronic conductor should also be sufficiently "open" that there is room for precipitated electroactive species to deposit on the matrix. Finally, any binder employed in the positive electrode should not prevent contact between the electronic conductor and the electroactive species. For example, the binder should not provide so much wetting that precipitated sulfur particles and/or the current collector are completely wetted and therefore unable to exchange electrons.

LIQUID ELECTROLYTES

It has now been discovered that the performance of lithium-sulfur batteries can be improved by employing electrolyte compositions designed to solubilize lithium sulfide and relatively low molecular weight polysulfides. The new electrolytes of this invention are in fact designed to keep more sulfur discharge products in solution and therefore available for electrochemical reaction. In general, the electrolyte compositions of this invention include one or more solvents that strongly coordinate lithium. These solvents are "ionophores" for lithium ions. Exemplary ionophores are podands, coronands, and cryptands as described in chapter 10 of the treatise "Lithium Chemistry, A Theoretical and Experimental Overview," Anne-Marie Sapse and Paul Von Rague Schleyer, Eds. John Wiley & Sons, New York (1995) which is incorporated herein by reference for all purposes. Chapter 10 was written by Bartsch et al. Podands are acyclic multidentate ligands. Common examples are glymes and polyethylene glycols. Coronands are monocyclic multidentate ligands. Common examples are crown ethers and substituted crown ethers. Cryptands are multicyclic multidentate ligands.

In a preferred embodiment, the electrolyte solvents of this invention include one or more compounds having an ethanediether linkage. They have the general formula $R_1(CH_2CH_2O)_nR_2$, where n ranges between 1 and 10 and R_1 and R_2 are different or identical alkyl or alkoxy groups (including substituted alkyl or alkoxy groups). Alternatively, R_1 and R_2 may together form a closed ring to form a crown ether for example. Examples of linear solvents include the glymes $(CH_3O(CH_2CH_2O)_nCH_3)$ and related oxides of the formula $(CH_2CH_2O)_n(CH_2O)_p$, where p ranges from about 1 to 50. Such ethoxy repeating unit compounds serve as lithium ion coordinating solvents. In a preferred embodiment, the main solvent is a

glyme having a value of n ranging between 1 and 6. In an especially preferred embodiment, the glyme is dimethoxyethane ($\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3$).

The batteries of this invention can operate at room temperature. However, the present invention also pertains to systems operating at temperatures slightly outside of the ambient. Obviously, the choice of operating temperature ranges can influence the preferred electrolyte for the batteries of this invention. For example, at relatively low operating temperatures, lower molecular weight electrolytes will be preferred, so the value of " n " in the above-described ethanediether compounds will be in the lower end of the 1-10 range. At higher temperatures, the opposite is true.

While the electrolyte solvents described above are a main component of the electrolytes of this invention, one or more cosolvents may be provided with them. If such cosolvents are employed, they are preferably chosen to solubilize lithium cations or sulfide/polysulfide anions. In certain preferred embodiments, crown ethers and/or cryptands are provided as cosolvents. In other preferred embodiments, donor or acceptor cosolvents may be employed. In a particularly preferred embodiment, the cosolvent is dioxolane. Preferred dioxolane-containing electrolytes are further described in US Patent Application No. 09/245,167, titled DIOXOLANE AS A COSOLVENT IN Li/Li₂S_x BATTERIES, filed on February 5, 1999, and having Nimon et al. as inventors. That document is incorporated herein by reference for all purposes.

Crown ethers are macrocyclic polyethers generally having repeating ethoxy and/or propoxy groups. Crown ethers with 3 to 20 oxygen atoms have been synthesized. They are typically made up of linked ethoxy units $(\text{CH}_2\text{CH}_2\text{O})_n$ as shown below. A general abbreviation used is $n\text{-C-}m$ where n is the ring size and m is the number of oxygen atoms in the ring.

Commercially available crown ethers which have application in this invention include 12-crown-4, 15-crown-5, 18-crown-6, and modified crowns such as dibenzo-18-crown-6. Crown ethers are known to be complexing agents which solubilize alkali metal cations in nonpolar solvents. 12-crown-4 is known to be specific for the lithium cation.

In substituted crown ethers, one or more of the hydrogen atoms are replaced with a hydrocarbon group that may be linear, branched, or aromatic. These hydrocarbon groups may, in turn, be substituted with halo (F, Cl, Br, I), nitrile (CN), nitro (NO₂), hydroxy (OH), and other common substituent groups. Examples are presented in chapter 10 of the above referenced "Lithium Chemistry" treatise.

Specific examples include dibenzo-14-crown-4, tetramethyl-12-crown-4, benzo-15-crown-5. Crown ethers may also be substituted with podand groups such as (-COCH₂CH₂OCH₃) to form podano-coronands or "lariat ethers."

In an alternative embodiment, the main solvent is a cryptand. Cryptands are also known to strongly complex with alkali metal cations. Structurally, they are similar to crown ethers but possess an additional (-XCH₂CH₂) bridge to create an additional ring. X may be an oxygen, nitrogen, or sulfur atom. Often X is nitrogen and the corresponding cryptands are described as containing two nitrogen atoms linked by three (CH₂CH₂O)_n bridges. These compounds are commonly identified by the number of oxygen atoms in each of the three bridges. Thus, a cryptand in which two of the bridges have n = 2 (two oxygen atoms) and a third bridge having n = 1 (one oxygen atom) is identified as [2.2.1]-cryptand.

One example of a general class of cosolvents is the donor solvents, which tend to solubilize cations and acceptor solvents which tend to solubilize anions. Donor solvents are characterized by high donor numbers DN. A desirable property of both donor and acceptor cosolvents used in this invention is a high dielectric constants, ϵ . Such solvents generally promote dissociation of an ionic solute or a contact ion-pair.

Generally, donor solvents are those solvents which can be characterize as Lewis bases (they may be aprotic solvents). Generally, these solvents are good at solvating cations such as lithium ions. Donor solvents promote the ionization of covalent compounds to form intimate (or contact) ion-pairs. The concept of a solvent donor number is further explained and exemplified in "Experimental Electrochemistry for Chemists," by Sawyer and Roberts, Jr., John Wiley & Sons, New York (1995). That reference is incorporated herein by reference for all purposes.

Suitable donor cosolvents include hexamethylphosphoramide, pyridine, N,N-diethylacetamide, N,N-diethylformamide, dimethylsulfoxide, tetramethylurea, N,N-dimethylacetamide, N,N-dimethylformamide, tributylphosphate, trimethylphosphate, N,N,N',N'-tetraethylsulfamide, tetramethylenediamine, tetramethylpropylenediamine, and pentamethyldiethylenetriamine. These assist in solvation of lithium ions.

Suitable acceptor solvents assist in solvation of the sulfide and polysulfide anions. Acceptor solvents are those solvents which can be characterized as Lewis acids (they may be protic or aprotic solvents) and promote solvation of anions. Examples include alcohols such as methanol, glycols such as ethylene glycol, and polyglycols such as polyethylene glycol, as well as nitromethane, trifluoroacetic acid, trifluoromethanesulfonic acid, sulfur dioxide, and boron trifluoride.

It should be understood that the electrolyte solvents of this invention may also include other cosolvents which do not necessary fall into the donor solvent and acceptor solvent classes. Examples of such additional cosolvents include sulfolane, dimethyl sulfone, dialkyl carbonates, tetrahydrofuran (THF), dioxolane, propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), butyrolactone, N-methylpyrrolidinone, dimethoxyethane (DME or glyme), and combinations of such liquids.

In general, the liquid electrolyte solvents of this invention include about 50 to 100% by weight of the main solvent (excluding salts) which is usually one or more podand such as the above-described ethanediether compounds. The balance will be one or more of the cosolvents listed above. More preferably, the electrolyte solvents include about 50 to 100% by weight main solvent, and most preferably between about 70 and 90% by weight main solvent. As noted, the main solvent is one or more of the lithium coordinating ionophores described above (podands such as glymes, coronands such as crown ethers, or cryptands). Aside from the main solvent, the electrolyte solvent may include one or more cosolvents (described above) which make up the balance. In a particularly preferred embodiment, the electrolyte solvent includes DME as the main solvent and dioxolane as the cosolvent, with the dioxolane making up between about 5 and 15% by volume of the mixture.

Exemplary but optional electrolyte salts for the battery cells incorporating the electrolyte solvents of this invention include, for example, lithium trifluoromethanesulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$), lithium triflate (LiCF_3SO_3), lithium perchlorate (LiClO_4), LiPF_6 , LiBF_4 , LiAsF_6 , as well as, corresponding salts depending on the choice of metal for the negative electrode, for example, the corresponding sodium salts. As indicated above, the electrolyte salt is optional for the battery cells of this invention, in that upon discharge of the battery, the metal sulfides or polysulfides formed can act as electrolyte salts, for example, $\text{M}_{x/z}\text{S}$ wherein $x = 0$ to 2 and z is the valence of the metal.

Regardless of whether the sulfur is present in a solid phase, the cells of this invention preferably operate with their electrolytes at a concentration of between about 3 and 30 molar sulfur, more preferably between about 5 and 25 molar sulfur, and most preferably between about 10 and 20 molar sulfur. The sulfur used in this measure is the sulfur atoms in electroactive species. Thus, for example, one molar Li_2S corresponds to one molar sulfur, whereas one molar Li_2S_5 corresponds to five molar sulfur, and one molar S_8 corresponds to eight molar sulfur. Note that in some

cases at least some of the sulfur may exist as a suspended particles within the catholyte.

It should be understood that some systems employing liquid electrolytes are commonly referred to as having "polymer" separator membranes. Such systems are considered liquid electrolyte systems within the context of this invention. The membrane separators employed in these systems actually serve to hold liquid electrolyte in small pores by capillary action. Essentially, a porous or microporous network provides a region for entraining liquid electrolyte. As mentioned above, such separators are described in US Patent No. 3,351,495 assigned to W. R. Grace & Co. and US Patent Nos. 5,460,904, 5,540,741, and 5,607,485 all assigned to Bellcore, for example.

POSITIVE ELECTRODE

The positive electrode must utilize an electrochemically active material capable of being reduced during discharge by reaction with metal ions from the negative electrode. In this invention, the electrochemically active material includes some substantial fraction of "sulfur." This does not mean that the positive electrode must rely exclusively upon sulfur for its electrochemical energy, but often this will be the case.

As mentioned, the electroactive sulfur in the positive electrode may be referred to as "active sulfur" which represents sulfur that is elemental or would be elemental in a theoretically fully charged state of the battery. The sulfur of the positive electrode may be defined another way: at least one of elemental sulfur, a sulfide of the metal from the negative electrodes, and a polysulfide of the metal from the negative electrode. These definitions capture positive electrodes in various states of charge. For example, even if the fully charged cell includes only elemental sulfur, a slightly discharged cell will have some of its elemental sulfur reduced to a metal polysulfide or metal sulfide. Further, the theoretically fully charged state of some cells of this invention need not require that the positive electrode be entirely converted to elemental sulfur. It may be possible in some cases to have the positive electrode be a highly oxidized form of lithium polysulfide, for example, as in Li_2S_x where x is five or greater. The fully charged positive electrode may also include a mixture of such polysulfides together with elemental sulfur and possibly even some sulfide. It should be understood that during charge, the positive electrode would generally not be of

uniform composition. That is, there will be some amount of sulfide, sulfur, and an assortment of polysulfides with various values of x.

Some or all of the active sulfur components may be dissolved in the electrolyte solvent. If the active sulfur is totally dissolved, then the solid phase structure of the positive electrode simply contains an electronic conductor and possibly some binder or other additive. The sulfur is provided by the solution for reaction at the positive electrode electronic conductor.

Solid phase sulfur positive electrodes of this invention preferably include an electronic conductor in intimate contact with the electrochemically active sulfur. The electrochemically active material must also be in intimate contact with an ion conductor. In the above referenced Chu patents, the ionic conductor typically was a separately added gel or solid state material present in the positive electrode. In the liquid electrolyte batteries of the present invention, the ionic conductor is preferably the electrolyte itself which permeates through the positive electrode and thereby remains in intimate contact with the sulfur (elemental sulfur, metal polysulfides, and/or metal sulfides).

Exemplary electronically conductive materials of the composite positive electrode include carbon black, graphite, carbon fibers, electronically conductive compounds with conjugated carbon-carbon and/or carbon-nitrogen double bonds, for example but not limited to, electronically conductive polymers, such as, polyaniline, polythiophene, polyacetylene, polypyrrole, and combinations of such electronically conductive materials. The electronically conductive materials of the positive electrode may also have electrocatalytic activity.

As mentioned above, the electronic conductor in the positive electrode preferably forms an interconnected matrix so that there is always a clear current path from the positive current collector to any position in the electronic conductor. This provides high availability of electroactive sites and maintained accessibility to charge carriers over repeated cycling. Often such electronic conductors will be fibrous materials such as a felt or paper. Examples of suitable materials include carbon papers from Lydall Technical Papers Corporation of Rochester, NH, graphite felts available from Electrosynthesis Company of Lancaster, NY, and carbon whiskers available from Applied Sciences Inc. Carbon whiskers have a very large aspect ratio. Whisker diameter is on the order of 100nm with a length of about 1um. They can be coated from a whisker containing slurry onto aluminum foil or impregnated or sprayed into a network structure such as carbon paper. In the case of whiskers spray coated

onto carbon paper, the whiskers adhere to the carbon fiber surface, creating a multi-porous highly conductive structure.

The sulfur is preferably uniformly dispersed in a composite matrix containing an electronically conductive material. Preferred weight ratios of sulfur to electronic conductor in the sulfur-based positive electrodes of this invention in a fully charged state are at most about 50:1, more preferably at most about 10:1, and most preferably at most about 5:1. The sulfur considered in these ratios includes both precipitated or solid phase sulfur as well as sulfur dissolved in the electrolyte. Preferably, the per weight ratio of electronic conductor to binder is at least about 1:1 and more preferably at least about 2:1.

The composite sulfur-based positive electrode may further optionally include performance enhancing additives such as binders, electrocatalysts (e.g., phthalocyanines, metallocenes, brilliant yellow (Reg. No. 3051-11-4 from Aldrich Catalog Handbook of Fine Chemicals; Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, Milwaukee, WI) among other electrocatalysts), surfactants, dispersants (for example, to improve the homogeneity of the electrode's ingredients), and protective layer forming additives to protect a lithium negative electrode (e.g., organosulfur compounds, phosphates, iodides, iodine, metal sulfides, nitrides, and fluorides). Preferred binders (1) do not swell in the liquid electrolyte and (2) allow partial but not complete wetting of the sulfur by the liquid electrolyte. Examples of suitable binders include Kynar available from Elf Atochem of Philadelphia, PA, polytetrafluoroethylene dispersions, and polyethylene oxide (of about 900k molecular weight for example). Other additives include electroactive organodisulfide compounds employing a disulfide bond in the compound's backbone. Electrochemical energy is generated by reversibly breaking the disulfide bonds in the compound's backbone. During charge, the disulfide bonds are reformed. Examples of organodisulfide compounds suitable for use with this invention are presented in US Patents Nos. 4,833,048 and 4,917,974 issued to DeJonghe et al. and US Patent No. 5,162,175 issued to Visco et al.

METHODS OF MAKING A POSITIVE ELECTRODE

As mentioned, an important feature of this invention is the ability to provide electrodes having electroactive material (usually sulfur) in intimate contact with an electronic conductor. This facilitates electron transport to and from the active material to allow nearly complete utilization of the active material. Note that good utilization

also requires that ions be readily available to the sulfur. This criterion is met by ensuring that, during operation, any solid sulfur in the positive electrode is in intimate contact with the liquid electrolyte (which provides a necessary ionically conductive medium). Thus, the positive electrode should be made sufficiently permeable to the liquid electrolyte that most all the sulfur contacts electrolyte. If the sulfur is present only in the dissolved state (as catholyte), then the positive electrode is simply the electronically conductive material and possibly some binder and other additives. Such positive electrode should provide good contact with the catholyte to ensure rapid charge transfer between the solid and liquid phases.

Some relevant details of processes for fabricating positive electrodes suitable for use with this invention are provided in US Patent No. 5,582,623 (previously incorporated herein by reference). Much discussion in that application focused on three-part positive electrodes, which include a gel or solid-state ionic conductor in addition to the sulfur and electronic conductor. The positive electrodes used with the present invention rely on the electrolyte itself as the ionic conductor, and therefore do not require a separate ionic conductor. Nevertheless, the fabrication details provided in the '623 patent are generally applicable to the electrodes employed in the present invention.

One process for making positive sulfur-based electrodes suitable for use with this invention is outlined in the flow chart of Figure 2. A process 300 begins at 302 and then, in a step 304, a slurry is prepared from a liquid and at least some of the positive electrode components. The solid components of the slurry may include active sulfur, an electronic conductor, a dispersing agent, and a binder. After the slurry is formed, it is coated onto a substrate such as a current collector or carbon paper electronic conductor matrix. See step 306. At this point, the slurry liquid may be removed by any number of processes including evaporation. The resulting "preformed positive electrode" may then be treated at a step 308 according to a post coating process such as heating to bind the various solid phase electrode components. At the conclusion of step 308, a completed electrode has been produced. Then, at a step 310, the completed electrode is assembled into a battery cell, with the process being complete at 312.

During process 300, sulfur may be introduced into the positive electrode at various points as indicated by optional steps 350, 352, and 354. The sulfur may be introduced in at least one of these steps. At step 350, sulfur is optionally introduced as one of the solid components to the slurry prepared at step 304. Introduction of sulfur at step 350 is referred to as a "Type I" process. At step 352, sulfur may be

introduced during electrode treatment step 308. This is referred to herein as a "Type II" process and typically involves providing a concentrated solution of elemental sulfur, polysulfide, sulfide, or combination thereof to the preformed electrode. Finally, at step 354, sulfur may be introduced to the electrode during cell assembly (step 310) in a "Type III" process. In this case, the sulfur (as elemental sulfur, polysulfide, sulfide, or combination thereof) is provided in a concentrated electrolyte solution or suspension. It is important to recognize that the sulfur may be added to the electrode at any or more of steps 350, 352, and 354.

In slurry preparation step 304, the procedure should produce a uniform slurry, in which the solids are dispersed, stabilized and de-agglomerized. Details of a particular slurry preparation depends on the type and weight percents of the solids content as well as the type and amount of liquid solvent employed. There are, however, some general procedures that are typical for many of the slurry preparations.

A slurry typically includes solids dispersed and/or dissolved in a liquid phase. Solid slurry components may include an electronically conductive material, a binding agent, a dispersing agent, a solid state and/or gel state ionic conductor, and active sulfur (if any). Typically the solids content in the slurry is uniformly dispersed throughout the liquid phases, but some, all, or none of the solids may be dissolved in the liquid phases.

In a first method of slurry preparation, the active sulfur (if any), the electronically conductive material, and a dispersing agent are stir-mixed in an appropriate solvent until a uniform dispersion is formed. In a preferred embodiment, a dispersing agent is not added to the slurry as it provides no function in the final product and merely adds weight. The ratio of milliliters of solvent to grams of solid material depends on the desired composition and texture of the slurry. Some ranges for the liquids and solids weight percents are presented in the Table shown in Figure 3. Once the dispersion is uniformly mixed, the binding agent is gradually added to the dispersion in a step wise fashion while the dispersion is continuously stir-mixed. The gradual addition of the binding agent combined with continuous stir mixing of the dispersion helps to prevent flocculation and the creation of grossly large aggregates. The slurry is made uniform by stir mixing for a period of at least 24 hours followed by placing the slurry through a three roll mill.

In a second method of slurry preparation, the active sulfur (if any), the electronically conductive material and the dispersing agent are stir mixed in an appropriate solvent until the dispersion is uniform. This dispersion is known as dispersion #1. In a preferred embodiment, the dispersing agent is not added to the

slurry. The binding agent is added to an appropriate solvent in order to make a second dispersion, known as dispersion #2. Dispersion #2 is also stir mixed until it becomes uniform. Dispersion #2 is then slowly added to dispersion #1 while Dispersion #1 undergoes continuous stir-mixing. The slurry is stir mixed for 24 hours and then put
5 through a three roll mill to make it more uniform.

Representative electronically conductive materials used in the slurry include carbon blacks, graphites, carbon fibers and whiskers, electronically conductive compounds with conjugated carbon-carbon and/or carbon-nitrogen double bonds, for example but not limited to electronically conductive polymers, such as polyaniline,
10 polythiophene, polyacetylene, polypyrrole, and combinations of such electronically conductive materials. The electronically conductive material in the slurry provides a mechanism for electron transfer and for electronic conduction throughout the positive electrode. The weight percent of electronically conductive material in the solids content of the slurry typically ranges from 15%-85%, but can be as high a 100%.

15 Representative binding materials that in part comprise the slurry include but are not limited to polymeric materials, such as polyethylene oxide, polyvinylidene fluoride, polyethylene, polytetrafluoroethylene, electronically conductive polymers, such as polyaniline, polythiophene, polyacetylene, polypyrrole, and combinations of such polymeric materials. The binder may be added to the slurry to enhance
20 dispersion of the solids in the slurry and/or to stabilize the solids in the slurry from segregation, aggregation and/or flocculation. The binder may also be added to enhance the mechanical integrity of the positive electrode, to improve mechanical and electrical contact at the solid-solid interface and/or the solid/liquid interface, to increase electronic and/or ionic conduction throughout the composite positive
25 electrode, and still further, to enhance the electrochemical redox reactions. The solids content weight percent of binding materials in the slurry typically ranges from 5%-50%, but can be as low as zero percent.

Representative dispersing agents that in part comprise the slurry include but are not limited to low molecular weight polyethylene glycols, soya lecithin, etc., and
30 such dispersing agents that are well recognized in the field. The solids content weight percent of dispersing agent in the slurry can be as high as 25% and as low as zero percent, but is typically 2%-10%.

Active sulfur may also be added to the slurry, and this type of sulfur loading is known as type I sulfur loading. The active sulfur added to the slurry includes but is
35 not limited to elemental sulfur, sulfides, polysulfides, redox sulfur polymers, and a combination of such sulfur-containing materials.

Liquid phases are typically added to the slurry and can act as vehicles to better disperse, de-agglomerate and or dissolve the solids content. Typical liquid phases include but are not limited to acetonitrile, iso-propyl alcohol, tetrahydrofuran, carbon disulfide, tetraglyme, dibutyl phthalate and acetone.

5 Cathodes may be coated from the slurry (at step 306) using several variations of a Mayer rod method or using spray coating or other suitable method. In order to make uniform, crack free coatings that remain adhered to the current collector, special attention must be given to the coating process, especially when trying to formulate thicker cathode coatings on a flat sheet current collector. The following methods have
10 been found acceptable.

Method #1 -- This method is used for thin film coatings on a metallic current collector foil such as Al or stainless steel. A slurry is Mayer rod coated directly onto a metal current collector and the solvent is allowed to evaporate off. The thickness of the coating is controlled by the type of Mayer rod employed, the consistency of the
15 slurry, and the number of Mayer rod passes. For example, a coating thickness of 25 micrometers may be formed with a single pass of a Mayer rod having a wire diameter of 0.078 inches.

Method #2 -- This method is used for thicker film coatings on a metallic current collector foil such as Al or stainless steel. Method #2 is similar to that
20 described in Method #1, with the main difference being that the coatings are made with Mayer rods that have a pre-defined gap between the Mayer rod and the substrate. In a preferred embodiment, this gap ranges between about 0 and 200 micrometers.

Method #3 -- This method is used for impregnating slurry into carbon paper networks and carbon felt materials. In this method the slurry is vacuum impregnated
25 into a carbon paper. The carbon paper is placed on top of a silk screen that is molded to a vacuum plate. Slurry is impregnated into the carbon paper by Mayer rod coating while applying a vacuum to the backside of the carbon paper. The vacuum helps to load the slurry into the paper and allows for a more uniform distribution of slurry through the thickness of the paper. The amount of slurry inserted into the carbon
30 paper depends on the mesh size of the silk screen, the Mayer rod #, the viscosity of the slurry, and, of course, on the number of Mayer rod passes.

As mentioned, in Type II processes, active sulfur is introduced to the electrode during treatment step 308. After the slurry has been coated and dried, either on a flat metal sheet current collector or into a carbon paper network, it is considered a
35 preformed cathode. Preformed cathodes can be treated to a variety of different

procedures such as heat treatments, chemical treatments, etc. Possible chemical treatments serve to load additives and/or active sulfur to the cathode. One method for adding active sulfur to the cathode is to dissolve elemental sulfur in an appropriate highly volatile solvent and then to re-crystallize the sulfur on the surface of the preformed cathode. Of course, the active sulfur may remain in solution for liquid format batteries.

There are certain advantages of loading sulfur into a preformed cathode in this manner. For example, the electronically conductive network can be formed and optimized such that during sulfur dissolution the electronically conductive network does not break apart under the associated stresses.

The final cell assembly (step 310) may be performed in various manners. One part of the final cell assembly is to insert electrolyte into the cathode structure. If the electrolyte contains dissolved active sulfur, the sulfur loaded during this step is considered to be Type III sulfur loading. Care must be taken that the electrolyte remains within the confines of the cathode. Too much liquid in the battery cell can lead to a detrimental loss of active sulfur away from the carbon electrode. On the other hand, enough electrolyte must be added to the cathode to allow for a continuous pathway for the dissolved sulfur species to move away and then back to the redox sites in the cathode. Moreover, care must be taken to make sure that there is an adequate ionic pathway through the cathode, through the separator, and to the surface of the anode. The method used to insert the electrolyte into the cathode will depend strongly on the pore structure of the cathode and on the volatility of the liquid electrolyte. In general, the less volatile is the electrolyte, the more readily the electrolyte can be loaded into the cathode. On the other hand, volatile solvents typically have lower viscosity and as such may penetrate the cathode pore structure more effectively. The catholyte may be vacuum impregnated into the positive electrode as follows. First, place the catholyte on the electrode. Then, pull a vacuum under the electrode for several minutes. Finally, remove the vacuum.

While the above described process has been described in terms of batchwise steps, it will be apparent to those of skill in the art that many steps of the process may also be performed in a continuous fashion as described in the above-referenced US Patent No. 5,582,623.

NEGATIVE ELECTRODE

Most generally, the negative electrode can comprise any metal, any mixture of metals, glass, carbon or metal/carbon material capable of functioning as a negative electrode in combination with the sulfur-based composite positive electrode of this invention. Accordingly, negative electrodes comprising any of the alkali or alkaline earth metals or transition metals (the polyether electrolytes are known to transport divalent ions such as Zn^{++}), for example, in combination with the positive electrodes and electrolytes of this invention are within the ambit of the invention, and particularly alloys containing lithium and/or sodium.

Stated another way, the negative electrodes employed in the batteries of this invention may include a metal (in elemental or alloy form) or an ion of that metal as used in, for example, a carbon intercalation electrode or a glass matrix electrode. As explained above, metal ions from this negative electrode combine with elemental sulfur or polysulfides to produce a sulfide and polysulfides of the metal during discharge of the battery. Some of the resulting metal sulfides and polysulfides may remain localized near the positive electrode. Some fraction of these discharge products, however, will dissolve in the solvent of the electrolyte and move freely through the liquid containing regions of the cell. As mentioned, some of these dissolved discharge products may actually precipitate from solution and become unavailable for further electrochemical reaction, thereby reducing the cell's capacity. The present invention addresses this problem.

In one preferred embodiment, the materials for the negative electrodes include a metal such lithium or sodium or an alloy of one of these with one or more additional alkali metals and/or alkaline earth metals. Preferred alloys include lithium aluminum alloys, lithium silicon alloys, lithium tin alloys, and sodium lead alloys (e.g., Na_4Pb). Other metallic electrodes may include alkaline earth electrodes such as magnesium and their alloys; transition metal electrodes such as aluminum, zinc, and lead and their alloys;

The surface of such metallic negative electrodes can be modified to include a protective layer on the electrolyte side. This protective layer should be conductive to lithium ions and help prevent the formation of lithium dendrites or "mossy" lithium on repeated cycling. It can be produced by the action of additives, including organosulfur compounds, phosphates, iodides, nitrides, and fluorides. The protective layer may also be pre-formed from an inert physical barrier conductive to the metal ions from the negative electrode. Examples of such pre-formed protective layers include lithium phosphate, silicate glasses, polymers, or a combinations of these. In a particularly

preferred embodiment, the protective layer is poly(1-trimethylsilyl-1-propyne) ("PTMSP"). The protected negative electrodes may not require an electrolyte separator, thereby allowing the thin film cells of this invention to be made even thinner.

5 Examples of preferred protective layer formats and materials are described in the following US Patent applications, each of which is incorporated herein by reference for all purposes: US Patent Application No. 09/086,665, filed May 29, 1998, titled PROTECTIVE COATINGS FOR NEGATIVE ELECTRODES, and naming Visco et al. as inventors; US Patent Application No. 09/139,603, filed August 10 25, 1998, titled PLATING METAL NEGATIVE ELECTRODES UNDER PROTECTIVE COATINGS, and naming Chu et al. as inventors; US Patent Application No. 09/139,601, filed August 25, 1998, titled METHOD FOR FORMING ENCAPSULATED LITHIUM ELECTRODES HAVING GLASS PROTECTIVE LAYERS, and naming Visco et al. as inventors; and US Patent Application No. 15 09/431,190, filed November 1, 1999, titled ENCAPSULATED LITHIUM ALLOY ELECTRODES HAVING BARRIER LAYERS, and naming Chu et al. as inventors.

 In an alternative embodiment, the negative electrode may be an intercalation electrode such as a carbon-based lithium ion electrode. Such electrodes are available in commercial lithium ion batteries available from Sony Corporation of Japan. These 20 materials are described by Jeffrey Dahn in Chapter 1 of "Lithium Batteries, New Materials, Developments and Perspectives," edited by G. Pistoia and published by Elsevier (1994), which reference is incorporated herein by reference. Generally, such electrodes have the formula Li_yC_6 (where $y = 0.3$ to 2). For many of these materials, the fully charged electrode has the formula LiC_6 . The intercalation electrode matrix 25 may include graphite, petroleum coke, carbon inserted within highly disordered carbons, etc. The inserted carbon may also be doped with boron, phosphorus, or other appropriate dopant. In one example, the carbon may be prepared from low temperature pyrolysis (about 750°C) of carbon or carbon-silicon containing polymers such that the carbon product retains some hydrogen or silicon or both. (See, Sato et al., "A Mechanism of Lithium Storage in Disordered Carbons," Science, 264: 556 (22 30 April 1994), which discusses very good results with a preferred negative electrode of Li inserted within poly p-phenylene-based carbon).

 Glass matrix negative electrodes such as $\text{Li}/\text{Sn}_2\text{O}_3$ and Li/SiO_2 may also be employed in the batteries of the present invention. These electrodes are similar to the 35 above-described carbon-based intercalation electrodes in that lithium ions are inserted therein during charge and removed during discharge. Such glass matrix electrodes are

described in various references including Tahara et al., European Patent Application No. 93111938.2 (1993), Idota et al. Canadian Patent Application, 21134053 (1994), and I. Courtney et al. Meeting Abstracts of the Electrochemical Society, Fall Meeting, San Antonio, TX, Oct. 6-11, 1996 Vol. 96-2, Abstract # 66, page 88, each of which is
5 incorporated herein by reference for all purposes.

UTILIZATION AND PERFORMANCE

In many cases, the battery cells of this invention are rechargeable or secondary cells. Unlike primary cells which discharge only once, the secondary cells of this
10 invention cycle between discharge and charge at least two times. Typically, secondary cells of this invention will cycle at least 50 times, with each cycle having a sulfur utilization (measured as a fraction of 1675 mAh/g sulfur output during the discharge phase of the cycle) of at least about 10%. More preferably, at least 50 cycles will have a minimum sulfur utilization of at least about 20% (most preferably at least about
15 30%). Alternatively, the secondary cells of this invention will cycle at least two times, with each cycle attaining at least 50% utilization of sulfur in the positive electrode.

As used herein, "utilization" assumes that if all elemental sulfur in an electrode is fully utilized, the electrode will produce 1675 mAh/g of sulfur. That is, 100% utilization corresponds to 1675 mAh/g of the sulfur in the cell, and 10% utilization
20 corresponds to 167.5 mAh/g of sulfur in the cell.

As illustrated in the examples below, the technology described herein enables metal-sulfur cells to perform at levels unachievable in the prior art. In addition to the high utilization and long cycle life described above, cells of this invention may exhibit very high energy and power densities. Preferably, high energy density is attained
25 while allowing discharge at relatively high, commercially useful, rates. In a preferred embodiment, metal-sulfur cells have a laminate energy density of at least about 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². More preferably, the metal-sulfur cells have a laminate energy density of at least about 450 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². Following the
30 teachings of this invention, it is possible to fabricate cells having both the high laminate energy densities mentioned and laminate power densities in the region of 500 Watts/kilogram or higher. Such cells often find use as primary batteries.

Note that a "laminate" energy density is calculated by dividing the total energy obtained from the cell in a single cycle by the combined mass of the anode, cathode,

electrolyte and separator. The masses of the cell casing and any current collectors are not considered in the laminate energy density calculation. The "laminate power density" is obtained by dividing the total power obtained from the cell in a single cycle by the combined mass of the anode, cathode, electrolyte and separator. Again, the masses of the cell casing and any current collectors are not considered. The power density of a cell can be controlled by the rate of discharge. A higher rate of discharge generally provides a higher power density.

In a further preferred embodiment, the metal-sulfur cells have a laminate power density of at least about 200 Watts/kilogram, while maintaining a laminate energy density of at least about 40 Watt-hours/kilogram. Again, such cells often find use as primary batteries.

Regarding secondary metal-sulfur cells of this invention, they preferably maintain, over 10 more cycles, laminate power densities of at least about 10 Watts/kilogram and laminate energy densities of at least about 20 Watt-hours/kilogram. More preferably these laminate power and energies are maintained for at least about 100 cycles. The examples below show that metal-sulfur cells of this invention can maintain, over 10 or more cycles, laminate power densities of at about 40 Watts/kilogram in conjunction with laminate energy densities of at least about 50 Watt-hours/kilogram.

As mentioned, one of the benefits of using the electrolytes of this invention with lithium-sulfur cells is that they keep relatively insoluble sulfide and polysulfide discharge products in "circulation." The cathode constructions of this invention also serve the same purpose. This allows the capacity of the cell to remain high after repeated cycles.

It should be understood that using the electrolytes of this invention which solubilize sulfur discharge products to a great extent, "self-discharge" must be considered. That is, because the discharge products of the positive electrode are quite soluble in the electrolytes of this invention, they will automatically dissolve from the positive electrode and move to the negative electrode where they could be reduced chemically without producing electrical energy. Obviously, such self-discharged mechanism is to be avoided. One way of mitigating this effect is by providing a protective layer on the negative electrode which prevents these dissolved discharge products from reaching the negative electrode and thereby reacting with it. As mentioned above, such protective layers will generally conduct metal ions but not allow most other species from reaching the negative electrode. Again, examples of

protective layers include lithium phosphate, silicate glasses, polymers, or combinations of these.

EXAMPLES

5 The first 29 examples described herein are separated into 2 general types: primary and secondary. There are 19 primary examples and 10 secondary examples. The primary examples are differentiated between High Rate (HR) and High Energy Density (HED) examples. There are 3 High Rate examples (HR#1, HR#2, and HR#3), and there are 16 High Energy Density examples (HED #1, HED#2, etc). The
10 secondary examples are designated with "Cyc", for cycling. There are 10 secondary examples (Cyc #1, Cyc #2, etc).

Each example corresponds to a specific cathode (CAT-TY#), catholyte (C-LYTE-TY#) and cell type (CELL-TY#). Furthermore, each cathode type corresponds to a specific slurry type (SLY-TY#). A detailed description for each type follows.

15

Slurry

SLY-TY1 - The solids included ~70 wt% carbon black, ~25 wt% PEO (polyethylene oxide Mw=900K), and ~5 wt% Brij35. The solvent was acetonitrile. The solid content was approximately 6 % solids by total weight of slurry.

20 In a first 2 liter container, 45 grams of carbon black, 3.25 grams of Brij35 and 800ml of acetonitrile were stir-mixed, using a shearing blade, until a uniform dispersion was formed. In a second container, 16.25 grams of PEO were dissolved in 500ml of acetonitrile. The contents of the second container, dissolved PEO in acetonitrile, were gradually added to the first container while the first container was
25 continuously mixed with a shear blade. The slurry was then stir-mixed for approximately 4 hours and appeared uniform. Thereafter, the slurry was further homogenized by 3-roller milling.

SLY-TY2 - The solids included ~70 wt% carbon black and ~30 wt% PVdF (polyvinylidene fluoride Mw~250,000). The solvent was Dimethyl formamide
30 (DMF). The solid content was approximately 2 % solids by total weight of slurry.

3.5 grams of PVdF was stir-mixed, using a shearing blade, with 600ml DMF in a 800ml glass container until PVdF was totally dissolved in DMF. Thereafter, 8.2

grams of carbon black was added and the slurry was kept stirring for approximately 1.5 hours until the slurry appeared well mixed and uniform. Thereafter, the slurry was further homogenized using a Waring Commercial Blender.

5 SLY-TY3 - The solids included ~50% sulfur, ~28 wt% carbon black, ~20 wt% PEO (polyethylene oxide Mw=900K), and ~2 wt% Brij35. The solvent was acetonitrile. The solid content was approximately 11 % solids by total weight of slurry.

10 In a first 2 liter container, 42.67 grams of sublime sulfur, 23.90 grams of carbon black, and 400ml of acetonitrile were stir-mixed, using a shearing blade, until a uniform dispersion was formed. In a second container, 1.71 grams of Brij35 and 17.07 grams of PEO were dissolved in 400ml of acetonitrile. The contents of the second container, dissolved PEO and Brij35 in acetonitrile, were gradually added to the first container while the first container was continuously mixed with a shear blade. The slurry was then stir-mixed for approximately 4 hours and appeared uniform. Thereafter, the slurry was further homogenized by 3-roller milling.

15 SLY-TY4 - The solids included ~70 wt% carbon black, ~25 wt% PEO (polyethylene oxide Mw=900K), and ~5 wt% Brij35. The solvent was deionized water. The solid content was approximately 6 % solids by total weight of slurry.

20 The preparation process is similar to the one described in *SLY-TY1* except the slurry was milled using a colloid mill.

 SLY-TY5 - The solid content materials were ~70 wt% carbon whiskers, ~25 wt% PVdF (polyvinylidene flouride Mw~250,000), and ~5 wt% Brij35. The solvent was solvent was dimethyl formamide (DMF). The solid content was approximately 7 % solids by total weight of slurry.

25 In a first container, 1.4 grams of Brij35 and 350 ml of DMF were stir-mixed, using a shearing blade. Thereafter, 19.5 grams of carbon whiskers was added to the first container. The contents in the first container were stir-mixed for about 20 minutes and then placed in a blender for 15 minutes, until the whiskers appeared wetted and paste-like. The contents of the first container were then 3-roller milled. A second container having 7 grams of PVDF dissolved in 50ml of DMF, was added to the first container and stir-mixed for 3 hours. Thereafter the slurry was 3 roller milled.

Cathode Coating Methods

Method #1: Doctor blade coating

In this method, slurry was coated directly on a 25 μ m-thick Al foil substrate using a wireless Mayer-rod as doctor blade. Thickness of the coating was controlled by a pre-defined gap between the wireless Mayer-rod and the Al foil substrate.

5 *Method #2: Air Spraying*

Spray coating was performed with an airbrush. Network substrates such as carbon paper or Al foil substrates were coated by spray coating.

Method #3: Vacuum Impregnation

Vacuum impregnation method was used to coat carbon paper substrates. The carbon paper was placed on top of a silk screen that was molded to a vacuum plate. The slurry was impregnated into the carbon paper by Mayer rod coating while applying a vacuum to the backside of the carbon paper. The amount of slurry inserted into the carbon paper depended on the mesh size of the silk screen, the Mayer rod size number, the viscosity of the slurry, and the number of Mayer rod passes.

15

Cathode Description

CAT-TY1 - CAT-TY1 is a carbon paper type cathode loaded with carbonaceous slurry. It was prepared by coating method #3 using slurry SLY-TY1. Coating thickness was about 210 μ m with a weight of 3.4 mg/cm².

20 CAT-TY2 - CAT-TY2 is a carbon paper type cathode loaded with carbonaceous slurry. It was prepared by coating method #2 using slurry SLY-TY2. Coating thickness depends on slurry weight; see Table 2.

Table 2

Slurry weight (mg/cm ²)	Cathode weight (mg/cm ²)	Cathode thickness (μ m)
0.3	1.56	250
0.6	1.86	250

1.4	2.66	300
-----	------	-----

CAT-TY3 - CAT-TY3 is a carbon paper type cathode loaded with a carbonaceous-sulfur slurry. It was prepared by coating method #3 using slurry SLY-TY3. Coating thickness and sulfur loading depends on slurry weight; see Table 3.

5

Table 3

Slurry weight (mg/cm ²)	Cathode weight (mg/cm ²)	Cathode thickness (μm)	Theoretical mAh/cm ²
10.6	11.86	340	9
14.0	15.26	390	12
17.7	18.96	500	15

CAT-TY4 - CAT-TY4 is a carbonaceous cathode coated on aluminum foil. It was prepared by coating method #1 using slurry SLY-TY4. Coatings with three different thicknesses have been prepared; see Table 4.

10

Table 4

Slurry weight (mg/cm ²)	Cathode weight (mg/cm ²)	Cathode thickness (μm)
0.5	7.06	32
1.2	7.76	44
1.9	8.46	54

CAT-TY5 - This cathode is similar to CAT-TY3 except that a thicker carbon paper was employed. Typical cathode weight was 7.9mg/cm². Cathode thickness was about 350um.

5 CAT-TY6 - CAT-TY6 is a fibril carbonaceous cathode coated on aluminum foil. It was prepared by coating method #2 using slurry SLY-TY5. Typical cathode weight was 13mg/cm². Cathode thickness was about 250um.

Cell Description

10 CELL-TY1 - CELL-TY1 is a laboratory cell that includes a cell laminate having a single anode layer, a single separator layer and a single cathode layer. The anode was 125um thick lithium from Cypress Foote Mineral Company; the cathodes were of type CAT-TY1, CAT-TY2, CAT-TY3, and CAT-TY4; the separator was Celgard 2400 obtained from Hoechst Celanese Company. The cell laminate was sandwiched between two stainless steel current collectors. The cells were loaded with
15 electrolyte or catholyte in an argon filled dry box, and final cell assembly, including sealing the cells was also performed in an argon filled dry box. The cell was removed from the dry box after sealing and testing on Maccor Battery Testers of the type Maccor model Series 4000.

20 CELL-TY2 - CELL-TY2 is a fully packaged battery having a pouch cell configuration in which the battery was sealed from the atmosphere by a polymeric laminate material such as PE/Al foil/PE. The contents of the cell were stacked and/or folded layers of a cell laminate that includes an anode, separator, and cathode, and sometimes additionally included a cathode current collector and an anode current collector. The anode was 125 micrometer lithium foil from Cypress Foote Mineral
25 Company; the cathodes were CAT-TY1, CAT-TY2, CAT-TY3, and CAT-TY5; the separator was Celgard 2400 from Celgard Company. The cell tabs, which extended to the outside of the battery pouch, were made of stainless steel, copper, aluminum, and/or nickel. Dry cells were assembled in a dry room. Cells were filled with electrolyte and/or catholyte in an argon filled dry box. After loading with electrolyte
30 or catholyte the cells were vacuum-sealed. Cell capacity depended on the number of stacked or folded layers and the composition of the cathode and catholyte.

Catholyte/Electrolyte Description

Electrolyte included organic solvent(s) and supporting salt. Catholyte included organic solvent(s), active sulfur and, in certain formulations, supporting salt.

Table 5

Category	Molarity Sulfur	Molarity LiDTF	Solvents
C-LYTE-TY1	2.5	0.25	DME/DIOX (90/10 vol%)
C-LYTE-TY2	3.4	0.34	DME/DIOX (90/10 vol%)
C-LYTE-TY3	5.7	0.38	DME/DIOX (90/10 vol%)
C-LYTE-TY4	7.5	0.5	DME/DIOX (90/10 vol%)
C-LYTE-TY5	8	0	DME/DIOX (90/10 vol%)
C-LYTE-TY6	10	0	DME/DIOX (90/10 vol%)
C-LYTE-TY7	12	0	DME/DIOX (90/10 vol%)
C-LYTE-TY8	3	0.5	Tetraglyme
C-LYTE-TY9	3	0.5	Tetraglyme/DME (50/50 vol%)
E-LYTE	0	0.5	DME/DIOX (90/10 vol%)
C-LYTE TY10	13.5	0	DME/DIOX (90/10 vol%)

Note that the carbon black (100% compressed acetylene black) used in these examples was manufactured by Chevron Chemical Co. The carbon whiskers were manufactured by Applied Sciences, Inc. The Cathode Network Matrixes CP-035 and CP-050 were manufactured by Lydall Tech. Papers. CP-035 had a fiber diameter of 10 micrometers, a weight of 1.26 mg/cm^2 , a thickness of 210 micrometers and an open volume of 97%. CP-050 had a fiber diameter of 10 micrometers, a weight of 1.80 mg/cm^2 , a thickness of 320 micrometers and an open volume of 97%.

Regarding the cathode components, the sublimed sulfur, the Li_2S , and the LiDTF were all manufactured by Aldrich corporation. The lithium used in the anodes was 125 micrometers thick and manufactured by Cypress Foote Mineral Company.

Regarding the solvents, the deionized water was manufactured by VWR, the acetonitrile was manufactured by Spectrum, and the DMF, DME, 1,3 dioxolane, and tetraglyme were all manufactured by Aldrich.

For the binders, the PVDF was Kynar 741 manufactured by Elf Atochem and had a molecular weight of 240,000 ~ 275,000 and the PEO was manufactured by Aldrich and had a molecular weight of 900,000. The polyethylene glycol dodecyl ether dispersion material was manufactured by Fluka.

Other cell components included the separator Celgard 2400 from Hoechst Celanese and the aluminum current collector (cathode) 25 micrometer thick 1100 alloy manufactured by All Foils of Brooklyn Heights, Ohio. The stainless steel 321 was likewise manufactured by All Foils.

Figures 4 and 5 show the laminate energy density and laminate power density for various cells constructed with the components and processes described above. As mentioned, the laminate energy and power densities are calculated by dividing the total energy or power obtained from the cell in a single cycle by the combined mass of only the anode, cathode, electrolyte and separator. In Figures 4 and 5, the various cells are identified by the alphanumeric identifiers that follow.

Room Temperature Primary Cells

HR #1

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY1*, tested at room temperature and at 10 mA/cm^2 , yields 33 Wh/kg for the

battery, 55 Wh/kg for the laminate, 386 W/kg for the battery, and 655 W/kg for the laminate.

HR #2

- 5 Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY1*, tested at room temperature and at 20 mA/cm², yields 26 Wh/kg for the battery, 47 Wh/kg for the laminate, 747 W/kg for the battery, and 1320 W/kg for the laminate.

10 *HR #3*

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY1*, tested at room temperature and at 30 mA/cm², yields 26 Wh/kg for the battery, 49 Wh/kg for the laminate, 1056 W/kg for the battery, and 1849 W/kg for the laminate.

15

HED #1

Cell of type *CELL-TY2*, cathode of type *CAT-TY5*, 4.8 ml of catholyte type *C-LYTE-TY9*, tested at room temperature and at 0.1 mA/cm², yields 400 Wh/kg for the battery and 540 Wh/kg for the laminate.

20

HED #2

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 1.86 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY5*, tested at room temperature and at 1.0 mA/cm², yields 300 Wh/kg for the battery and 476 Wh/kg for the laminate.

25

HED #3

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY4*, tested at room temperature and at 1.0

mA/cm², yields 373 Wh/kg for the laminate.

HED #4

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
5 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 1.0
mA/cm², yields 445 Wh/kg for the laminate.

HED #5

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
10 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY7*, tested at room temperature and at 1.0
mA/cm², yields 384 Wh/kg for the laminate.

HED #6

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
15 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY4*, tested at room temperature and at 0.1
mA/cm², yields 373 Wh/kg for the laminate.

HED #7

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
20 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 0.1
mA/cm², yields 445 Wh/kg for the laminate.

HED #8

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
25 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY7*, tested at room temperature and at 0.1
mA/cm², yields 384 Wh/kg for the laminate.

HED #9

Cell of type *CELL-TY1*, cathode of type *CAT-TY3* with the weight of 11.86 mg/cm², 0.25 ml electrolyte of type *E-LYTE*, tested at room temperature and at 1.0 mA/cm², yields 281 Wh/kg for the laminate.

5

HED #10

Cell of type *CELL-TY1*, cathode of type *CAT-TY3* with the weight of 15.26 mg/cm², 0.25 ml of electrolyte type *E-LYTE*, tested at room temperature and at 1.0 mA/cm², yields 169 Wh/kg for the laminate.

10

HED #11

Cell of type *CELL-TY1*, cathode of type *CAT-TY3* with the weight of 18.96 mg/cm², 0.25 ml of electrolyte type *E-LYTE*, tested at room temperature and at 0.1 mA/cm², yields 136 Wh/kg for the laminate.

15

HED #12

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 0.35 ml of catholyte type *C-LYTE-TY10*, tested at room temperature and at 0.2 mA/cm², yields 517 Wh/kg for the laminate.

20

HED #13

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.86 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 2.0 mA/cm², yields 320 Wh/kg for the laminate.

25

HED #14

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.86 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 3.0

mA/cm², yields 237 Wh/kg of the laminate.

HED #15

5 Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.2 ml of catholyte of type *C-LYTE-TY3*, tested at room temperature and at 5.0 mA/cm², yields 77 Wh/kg for the battery, 131 Wh/kg for the laminate, 204 W/kg for the battery, and 343 W/kg for the laminate.

HED #16

10 Cell of type *CELL-TY1*, cathode of type *CAT-TY6*, 0.37 ml of catholyte type *C-LYTE-TY4*, tested at room temperature and at 1.0 mA/cm², yields 295 Wh/kg for the laminate

Room Temperature Secondary Cells

15 *Cyc #1*

Cell of type *CELL-TY1*, cathode of type *CAT-TY4* with the weight of 7.06 mg/cm², 0.035 ml of catholyte type *C-LYTE-TY8*, cycled at room temperature and at 0.1 mA/cm² discharge / 0.1 mA/cm² charge, yields 500 cycles at 27 Wh/kg for the laminate.

20

Cyc #2

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 8.4 ml of catholyte type *C-LYTE-TY4*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge, yields 30 cycles at 155 Wh/kg for the battery and 203 Wh/kg for the laminate.

25

Cyc #3

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.2 ml of catholyte type *C-LYTE-TY4*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm²

charge, yields 20 cycles at 133 Wh/kg for the battery and 222 Wh/kg for the laminate.

Cyc #4

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY2*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge, yields 100 cycles at 76 Wh/kg for the battery and 130 Wh/kg for the laminate.

Cyc #5

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY2*, cycled at room temperature and at 0.75 mA/cm² discharge / 0.25 mA/cm² charge with 0.74 mA/cm² discharge capacity cutoff, yields 430 cycles at 37 Wh/kg for the battery and 64 Wh/kg for the laminate.

Cyc #6

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY3*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge with 2.84 mA/cm² discharge capacity cutoff, yields 60 cycles at 90 Wh/kg for the battery and 156 Wh/kg for the laminate.

Cyc #7

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY3*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge with 20% capacity cutoff, yields 150 cycles at 61 Wh/kg for the battery and 104 Wh/kg for the laminate.

Cyc #8

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY3*, cycled at room temperature and at 1.0

mA/cm² discharge / 0.5 mA/cm² charge, yields 4 cycles at 170 Wh/kg for the battery and 297 Wh/kg for the laminate.

Cyc #9

- 5 Cell of type *CELL-TY1*, cathode of type *CAT-TY4* with the weight of 7.76 mg/cm², 0.045 ml of catholyte type *C-LYTE-TY8*, cycled at room temperature and at 0.1 mA/cm² discharge / 0.1 mA/cm² charge, yields 300 cycles at 43 Wh/kg for the laminate.

10 *Cyc #10*

Cell of type *CELL-TY1*, cathode of type *CAT-TY4* with the weight of 8.46 mg/cm², 0.06 ml of catholyte type *C-LYTE-TY8*, cycled at room temperature and at 0.1 mA/cm² discharge / 0.1 mA/cm² charge, yields 100 cycles at 56 Wh/kg for the laminate.

15

- As shown in Figure 4, primary cells of this invention discharged at low to moderate discharge rates (relatively low power densities) have very large laminate energy densities. As illustrated, cells of this invention may also be discharged at high rates (associated with high laminate power densities) for high power applications.
- 20 Typically, such cells have a somewhat lower laminate energy density.

- As shown in Figure 5, secondary cells of this invention of this invention have good laminate energy densities and laminate power densities even after numerous cycles. While many discharge/charge cycles can degrade the performance of a cell, many cells constructed in accordance with this invention maintain very good
- 25 performance over hundreds of cycles as shown in Figure 5.

- Other experiments were conducted to demonstrate the performance advantages provided by the various aspects of this invention. The results of a few such experiments are tabulated in Figure 6. It should be understood that the experiments described herein represent but a small sampling of all experiments on lithium-sulfur
- 30 liquid systems conducted by or under the direction of the inventors. The experiments are provided mainly to show the high level of performance that can be attained when following the guidelines presented herein.

Example 1

A cathode film was made by mixing 50 (wt)% elemental sulfur, 24% carbon black, 18% polyethylene oxide Mw=900k (PEO), 2% Brij, and 6% lithium-trifluoromethanesulfonimide, in a solution of acetonitrile (solvent to solids ratio, 20:1 by weight). The components were stir-mixed for approximately two days until the slurry is well mixed and uniform. Thin cathode film were cast directly onto stainless steel current collectors, and the solvent was allowed to evaporate at ambient temperatures. The resulting cathode film weighed approximately 0.0015 gm per cm².

The separator was a micro-porous polymeric sheet having a nominal thickness of 1 mil (Hoechst Celanese, Celgard 2400). The cathode film and microporous separator were vacuum dried overnight to remove moisture prior to transfer into the argon glovebox for final cell assembly.

65 microliter of the electrolyte, which was a 0.5 molar solution of lithium-trifluoromethanesulfonimide (3M Company of Charlotte, North Carolina) in tetraglyme, was placed on the cathode film followed by placement of the microporous separator on the cathode. An additional 90 microliter of electrolyte was then placed on the micro-porous separator. A 5 mil (125 micron) thick high purity lithium anode film (FMC/Lithco of Gastonia, NC) was then placed on the other side of the microporous separator sheet.

The cell was then evaluated at 25°C with a Series 4000 battery test system from Maccor Inc. of Tulsa OK. This cell was cycled to a constant capacity corresponding to delivering 180 mAh per gm of the sulfur in the cell, that is, a utilization of 11% of the sulfur. The rates used were 90 microamp/cm² for discharging and 40 microamp/cm² for charging to cutoff voltages of 1.8 and 3.2 volts, respectively. Figure 7 shows the end of discharge voltage of this cell after each recharge cycle. As evident from the graph the cell performance is very consistent and over 600 cycles have been obtained.

Example 2

A cathode film was made by impregnating a slurry identical to the one described in example 1 into a carbon fiber paper (Lydall Technical Papers, Rochester, NY), and the solvent was allowed to evaporate at ambient temperatures. (This cathode was a carbon paper impregnated with slurry such that sulfur loading is of type I (see "methods" section)). The resulting cathode film weighed approximately 0.0029

gm per cm² and was vacuum dried overnight prior to transfer into the argon glovebox for final cell assembly.

5 135 microliter of the electrolyte of a 0.5 molar solution of lithium-trifluoromethanesulfonimide in tetraglyme was placed on the cathode film followed by placement of the microporous separator on the cathode. The separator was identical to the one described in example 1. An additional 45 microliter of electrolyte was then placed on the other side of the micro-porous separator. A 5 mil (125 micron) thick lithium anode film (FMC/Lithco Gastonia, NC) was then placed on the micro-porous separator sheet. Once assembled, the cell was compressed at 2 psi.

10 The cell was tested under similar conditions as described in example 1. The rates used were 90 microamp/cm² for discharging and for recharging. Figure 8 shows the percent sulfur utilization of this cell after each recharge cycle. As evident from the graph the cell performance is very consistent and more than 70 recharge cycles have been obtained at a sulfur utilization of approximately 40%.

15 ***Example 3***

A cathode film similar to the one described in example 2 was made with a slurry composition of 70 (wt)% carbon black, 25% polyethylene oxide (PEO, Mw=900k) and 5% Brij. The resulting cathode film weighed approximately 0.0037 g/cm² and was vacuum dried overnight prior to transfer into the argon glovebox for final cell assembly. (This cathode was a carbon paper cathode impregnated with slurry; sulfur loading was of type III.)

25 Sulfur was added to the cathode by inserting 200 microliter of a tetraethylene glycol dimethyl ether solution containing 0.5 moles of lithium-trifluoromethanesulfonimide and approximately 3 moles of sulfur dissolved. After insertion of the dissolved sulfur into the cathode, the microporous separator (identical to the one described in example 1) was placed on the cathode. This was then followed by the placement of an additional 20 microliter of the above mentioned dissolved sulfur solution on the microporous separator. A 5 mil (125 micron) thick lithium anode film (FMC/Lithco Gastonia, NC) was then placed on the micro-porous separator sheet. Once assembled, the cell was compressed at 2 psi.

30 The cell was tested under similar conditions as described in example 1. The rates used were 500 microamp/cm² for discharging to a cutoff voltage of 1.5 V and 90 microamp/cm² for recharging. Figure 9 shows the percent sulfur utilization of this cell after each recharge cycle. As evident from the graph the cell performance is very

consistent and more than 70 recharge cycles have been obtained at a sulfur utilization of approximately 40%.

Example 4

A cell identical to the one in example 3 was tested under similar conditions as described in example 1 at a discharge rate of 90 microamp/cm². Figure 10 shows that the sulfur utilization of this cell is of approximately 60% for more than 35 recharge cycles.

Example 5

A cell similar to the one described in example 3, but having a cathode weight of 0.00197gm/cm² and 230 microliters of the dissolved sulfur solution (identical to the sulfur solution described in example 3) impregnated into the cathode, was tested under similar conditions as described in example 1. The rates used were 1000 microamp/cm² for discharging to a cutoff voltage of 1.5 V and 500 microamp/cm² for recharging. The total volume of catholyte added to the cell was 250 microliters. As evident from Figure 11 the cell performance is very consistent and more than 30 recharge cycles have been obtained at a sulfur utilization of approximately 30%.

Example 6

A cathode film similar to the one described in example 3 was made with a slurry composition of 80 (wt)% carbon black, and 20% by solids content weight of a teflon dispersion (DuPont Company of Wilmington, Delaware). (The cathode is similar to the one in example 3, except the cathode components are active sulfur, Teflon binder and carbon black, in this example there is no solid state ionic conductor or gelled ionic conductor. The sulfur loading is of Type III.) The resulting cathode film weighed approximately 0.0039 g/cm² and was vacuum dried overnight prior to transfer into the argon glovebox for final cell assembly. The cell performance is shown in Figure 12.

OTHER EMBODIMENTS

The foregoing describes the instant invention and its presently preferred embodiments. Numerous modifications and variations in the practice of this invention are expected to occur to those skilled in the art. For example, the invention may provide overcharge protection as described in US Patent Application No.

08/686,609, filed July 26, 1996, and entitled RECHARGEABLE POSITIVE ELECTRODES and US Patent Application No. 08/782,245, filed March 19, 1997, and entitled OVERCHARGE PROTECTION SYSTEMS FOR RECHARGEABLE BATTERIES. Such modifications and variations are encompassed within the
5 following claims.

All references cited herein are incorporated by reference for all purposes.

CLAIMS*What is claimed is:*

1. A battery cell comprising:
 - a) a negative electrode including a metal or an ion of the metal;
 - b) a positive electrode comprising an electronically conductive material; and
 - c) a liquid catholyte including a solvent and dissolved electrochemically active material comprising sulfur in the form of at least one of a sulfide of the metal and a polysulfide of the metal, wherein the battery cell is characterized by an energy density, calculated based upon a laminate weight, of at least about 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm².
2. The battery cell of claim 1, wherein the battery cell is a primary battery cell.
3. The battery cell of claim 1, wherein the liquid catholyte has a sulfur concentration of at least about 5 M.
4. The battery cell of claim 1, wherein the liquid catholyte has a sulfur concentration of at least about 7 M.
5. The battery cell of claim 1, wherein the liquid catholyte has a sulfur concentration of at least about 10 M.
6. The battery cell of claim 1, wherein the battery cell attains at least about 10% utilization at ambient temperature.
7. The battery cell of claim 1, wherein the battery cell attains at least about 20% utilization at ambient temperature.
8. The battery cell of claim 1, wherein the positive electrode comprises a layer having an average thickness of at least about 40 micrometers.
9. The battery cell of claim 1, wherein the solvent comprises an ether.
10. The battery cell of claim 9, wherein the ether is dimethoxyethane.
11. The battery cell of claim 9, wherein the solvent further comprises dioxolane.
12. The battery cell of claim 1, wherein the solvent further comprises dioxolane.
13. The battery cell of claim 1, wherein the electronically conductive material comprises at least one of carbon and an electronically conductive polymer.

14. The battery cell of claim 1, wherein the electronically conductive material comprises an interconnected matrix.

5 15. The battery cell of claim 1, wherein the negative electrode is an alkali metal electrode.

16. The battery cell of claim 15, wherein the negative electrode is a lithium metal electrode.

10 17. The battery cell of claim 1, wherein the negative electrode includes a protective layer that is conductive to ions of the metal and protects the electrode from attack by the electrolyte.

15 18. A rechargeable battery cell comprising:

a) a negative electrode including a metal or an ion of the metal;

b) a positive electrode comprising a mixture of an electronically conductive material; and

20 c) a liquid catholyte including a solvent and dissolved electrochemically active material comprising sulfur in the form of at least one of a sulfide of the metal and a polysulfide of the metal, wherein the rechargeable battery cell is characterized by at least one of the following criteria:

25 i) the battery cell attains at least about 10% utilization over at least fifty cycles, and

ii) the battery cell attains at least about 50% utilization over two or more cycles.

30 19. The battery cell of claim 18, wherein the battery cell attains at least about 30% utilization over at least fifty cycles.

20. The battery cell of claim 18, wherein the battery cell attains at least about 50% utilization over at least 10 cycles.

35 21. The battery cell of claim 18, wherein the battery cell attains at least about 50% utilization over at least 75 cycles.

40 22. The battery cell of claim 18, wherein the metal and a negative electrode is at least one of sodium and lithium.

23. The battery cell of claim 18, wherein the negative electrode is a lithium intercalation electrode.

45 24. The battery cell of claim 18, wherein the electronic conductor of the positive electrode is at least one of carbon and an electronically conductive polymer.

25. The battery cell of claim 18, wherein the liquid electrolyte solvent includes an ether.

26. The battery cell of claim 18, wherein the electronically conductive material comprises an interconnected matrix.

27. The battery cell of claim 18, wherein the cell discharges at an average
5 current density of at least about 0.5 mA/cm^2 over at least 50 cycles in criteria (i) and at least 2 cycles in criteria (ii).

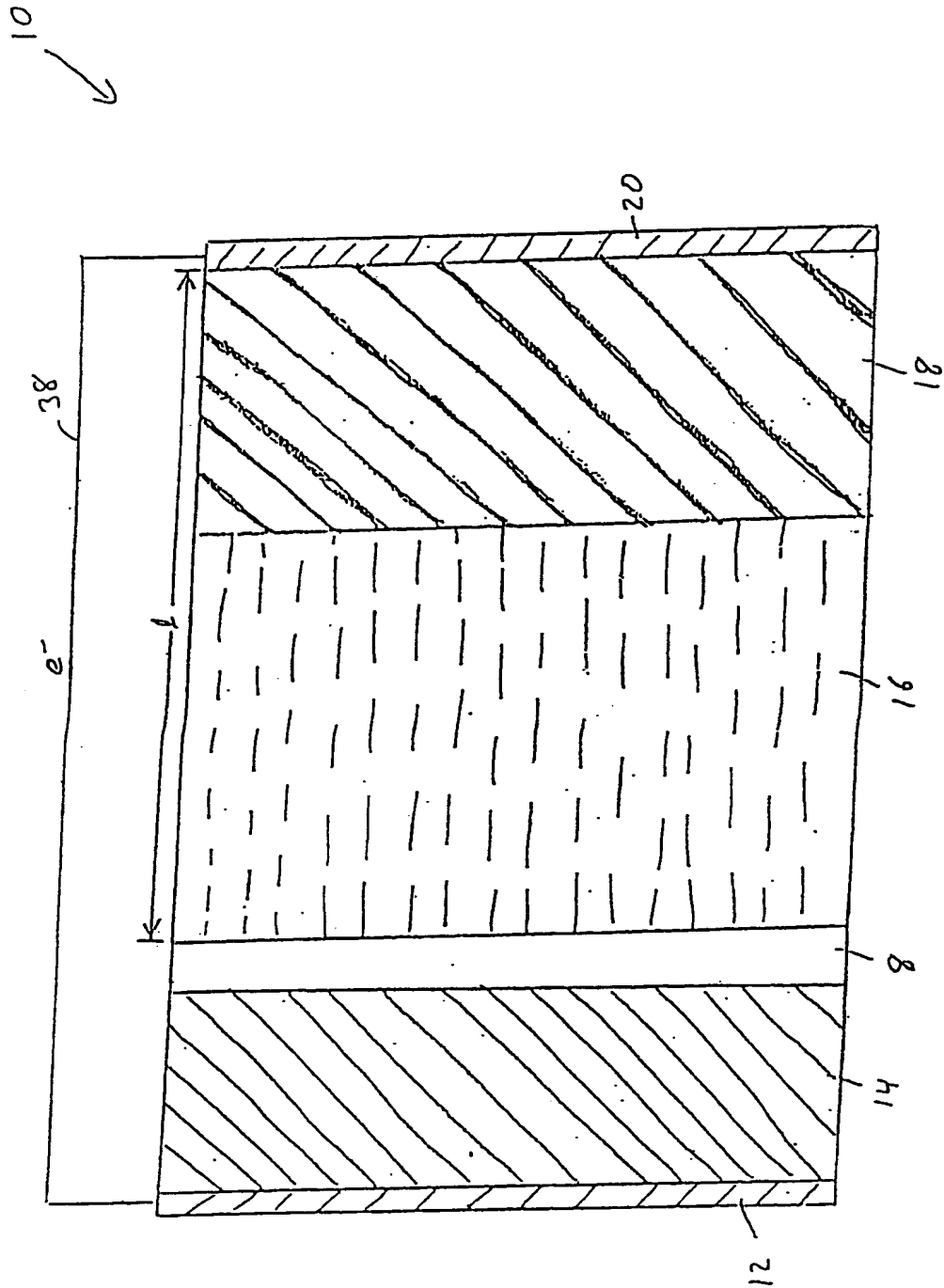


Figure 1

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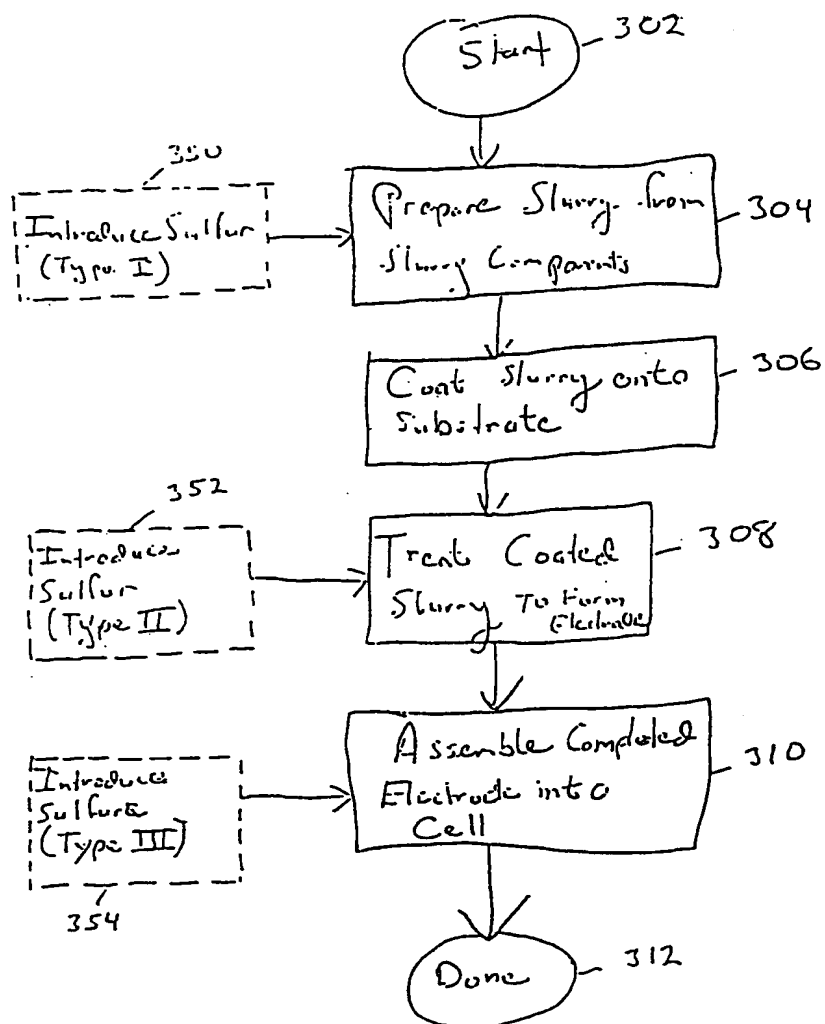


Figure 2

	electronically conductive material	wt%	binding agent	wt %	dispersing agent	wt %	active sulfur	wt %	electrolyte salt	wt %	liquid solvent	wt ratio of liquids to solids
slurry #1	acetylene black (Chevron)	24%	PEO, Mw=900k (Aldrich)	20%	Brij 35 (Aldrich)	2%	elemental (sublimed from Aldrich)	50%	Li-tri- fluoromethane sulfonimide, (HQ-115, 3M Company)	4%	Acetonitrile	50:1
slurry #2	acetylene black (Chevron)	10%	PEO, Mw=900k (Aldrich)	20%	Brij 35 (Aldrich)	5%	elemental (sublimed from Aldrich)	65%	none	NA	Acetonitrile	20:1
slurry #3	acetylene black (Chevron)	28%	PEO, Mw=900k (Aldrich)	20%	Brij 35 (Aldrich)	2%	elemental (sublimed from Aldrich)	50%	none	NA	Acetonitrile	20:1
slurry #4	acetylene black (Chevron)	70%	PEO, Mw=900k (Aldrich)	25%	Brij 35 (Aldrich)	5%	none	NA	none	NA	Acetonitrile	20:1
slurry #5	graphite flake (Asbury Graphite)	70%	PEO, Mw=900k (Aldrich)	25%	Brij 35 (Aldrich)	5%	none	NA	none	NA	Acetonitrile	20:1
slurry #6	XC-72 (Cabot)	70%	PEO, Mw=900k (Aldrich)	25%	Brij 35 (Aldrich)	5%	none	NA	none	NA	Acetonitrile	20:1
slurry #7	acetylene black (Chevron)	80%	Teflon™ (DuPont Company)	20%	none	NA	none	NA	none	NA	Isopropyl alcohol	30:1

Figure 3

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RT - Secondary

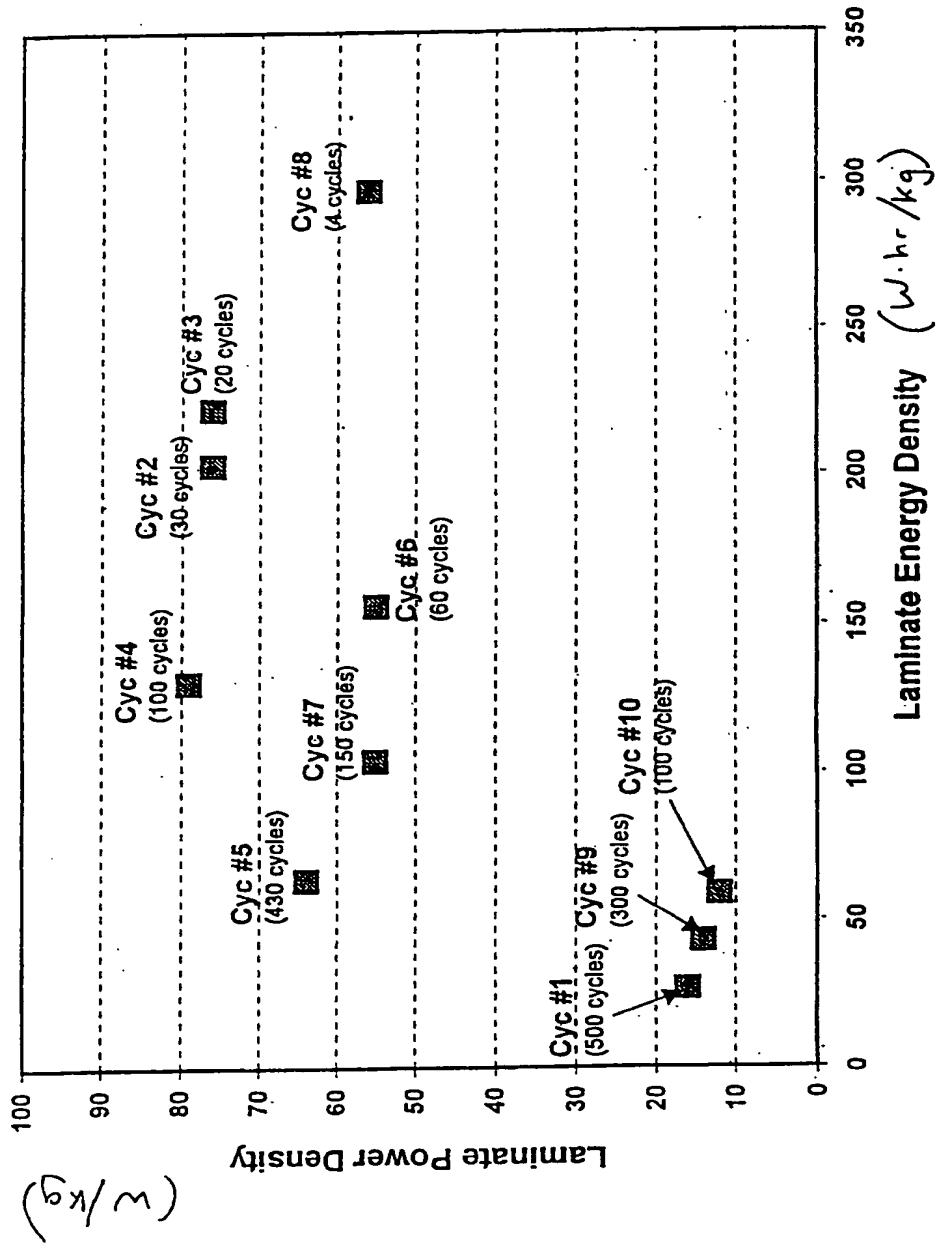


Figure 4

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RT - Primary

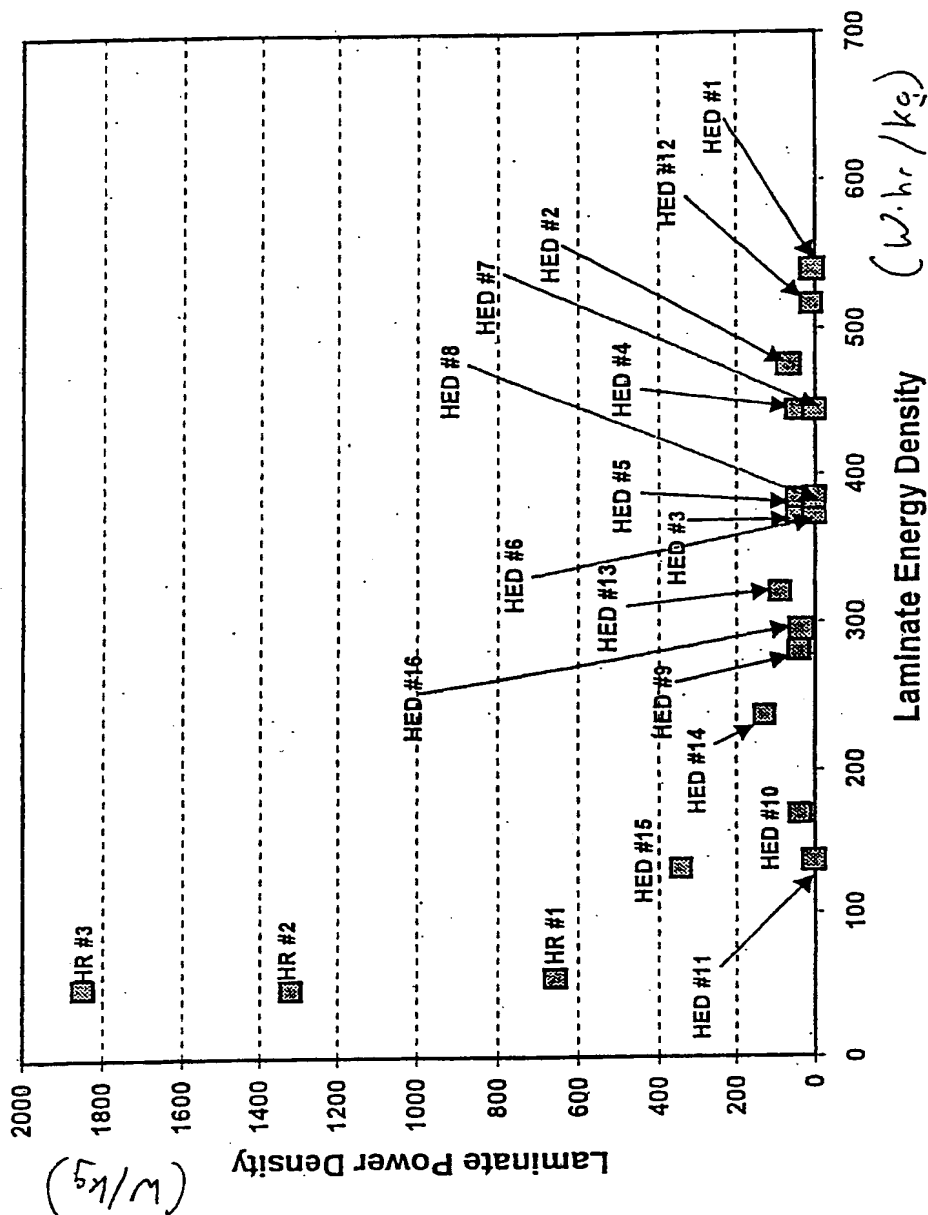


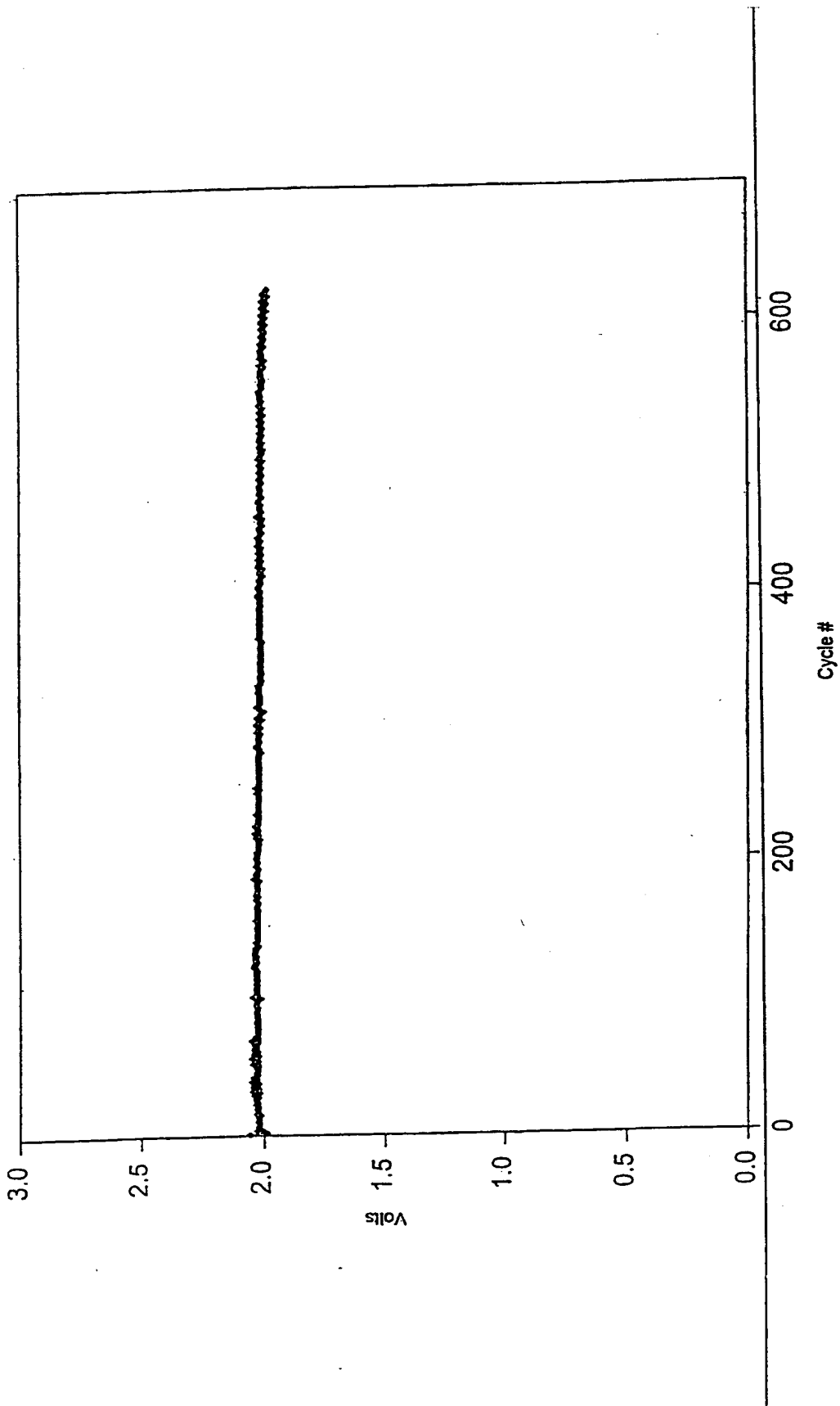
Figure 5

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Example	maximum % utilization	% utilization during cycling	Number of Cycles	discharge rate mA/cm ²
1	11%	11%	600+	~0.1
2	~55%	~40%	70+	~0.1
3	~50%	~40%	70+	0.5
4	65%	~60%	35+	~0.1
5	~35%	~30%	30+	1.0
6	50%	~40%	50+	0.5

Figure 6

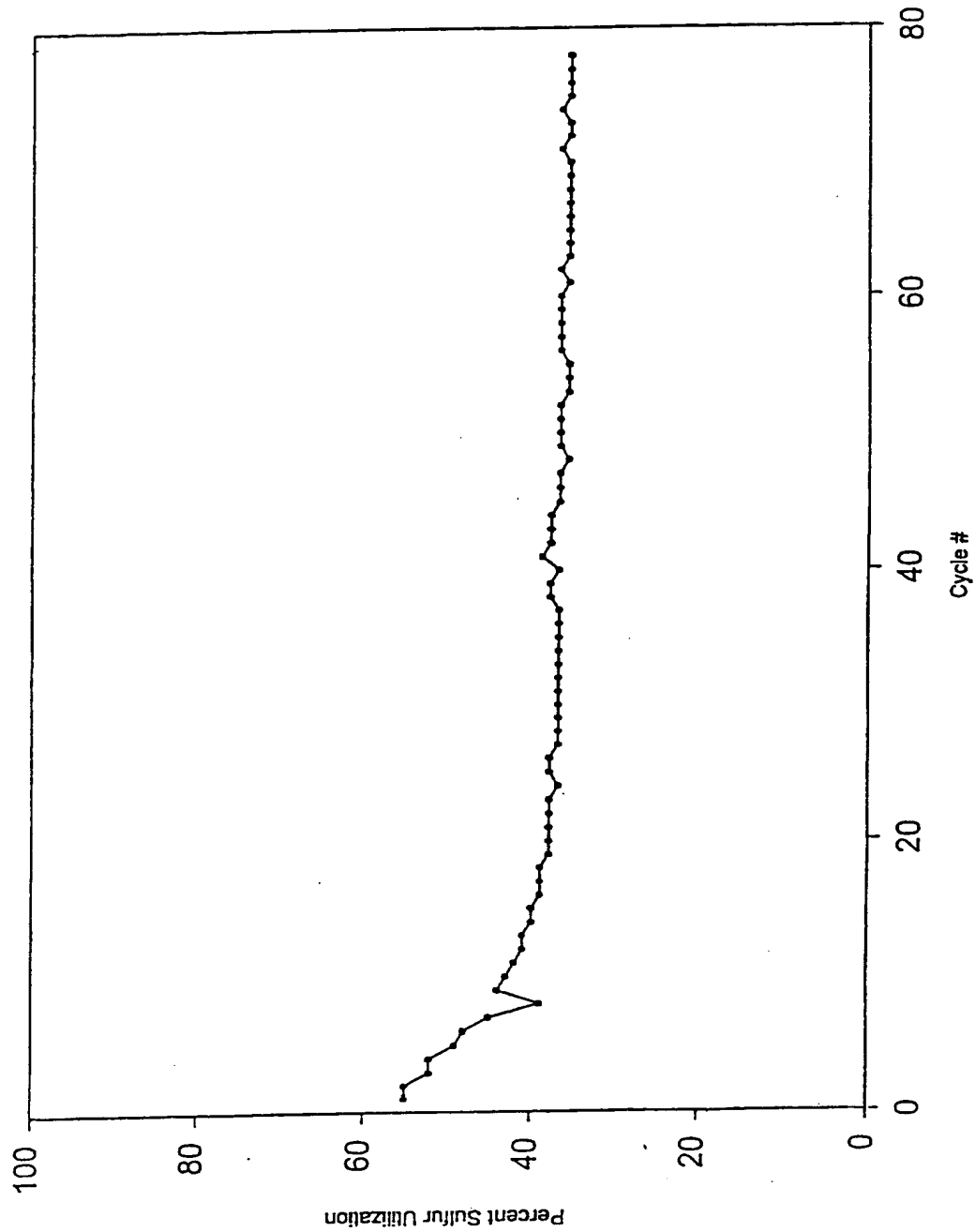
7/12



End of discharge voltage vs number of recharge cycles (11% Sulfur Utilization, 25°C).

Figure 7

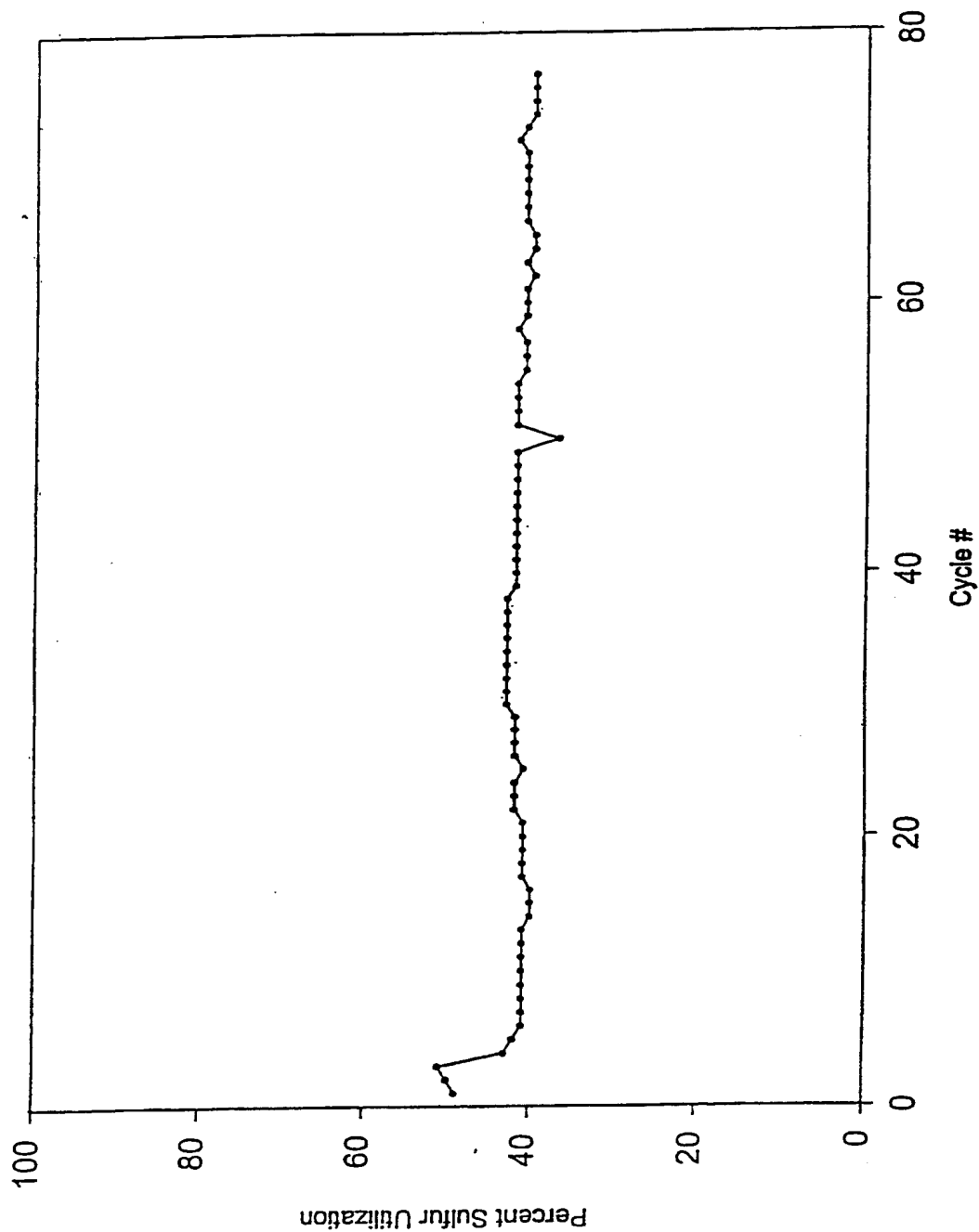
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Percent Sulfur Utilization vs. number of recharge cycles (25°C)

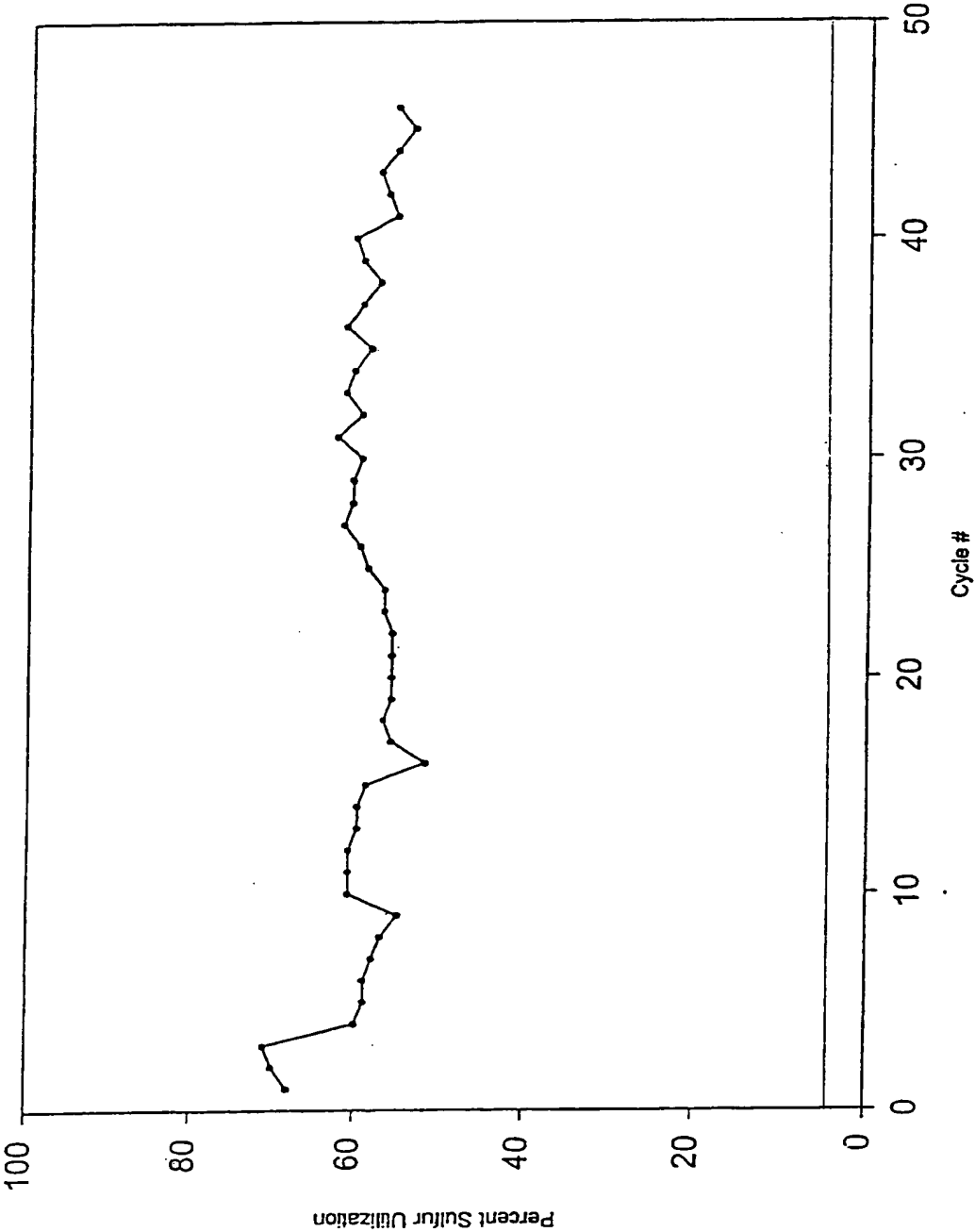
Figure 8

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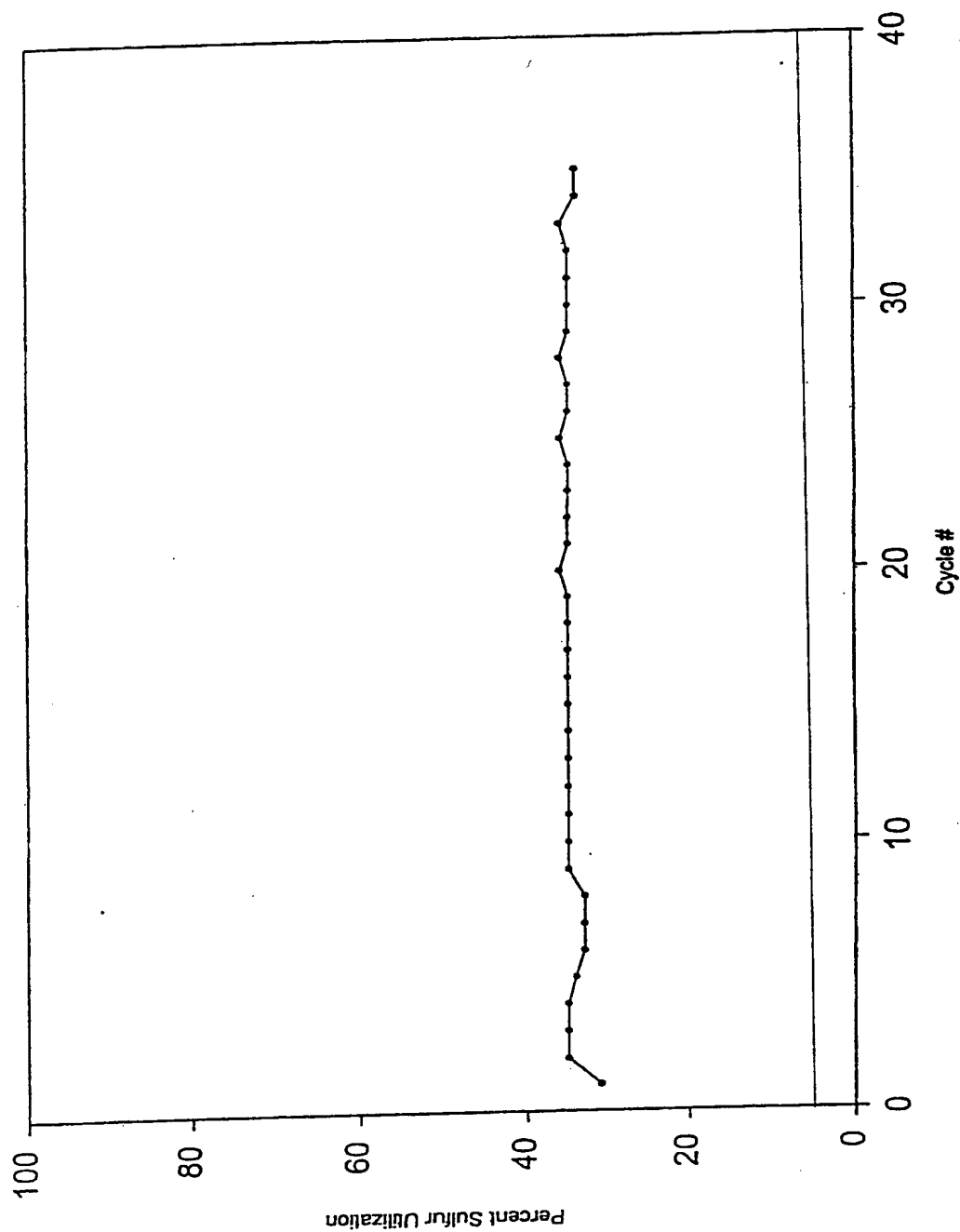


Percent Sulfur Utilization vs. number of recharge cycles (25°C)

Figure 7



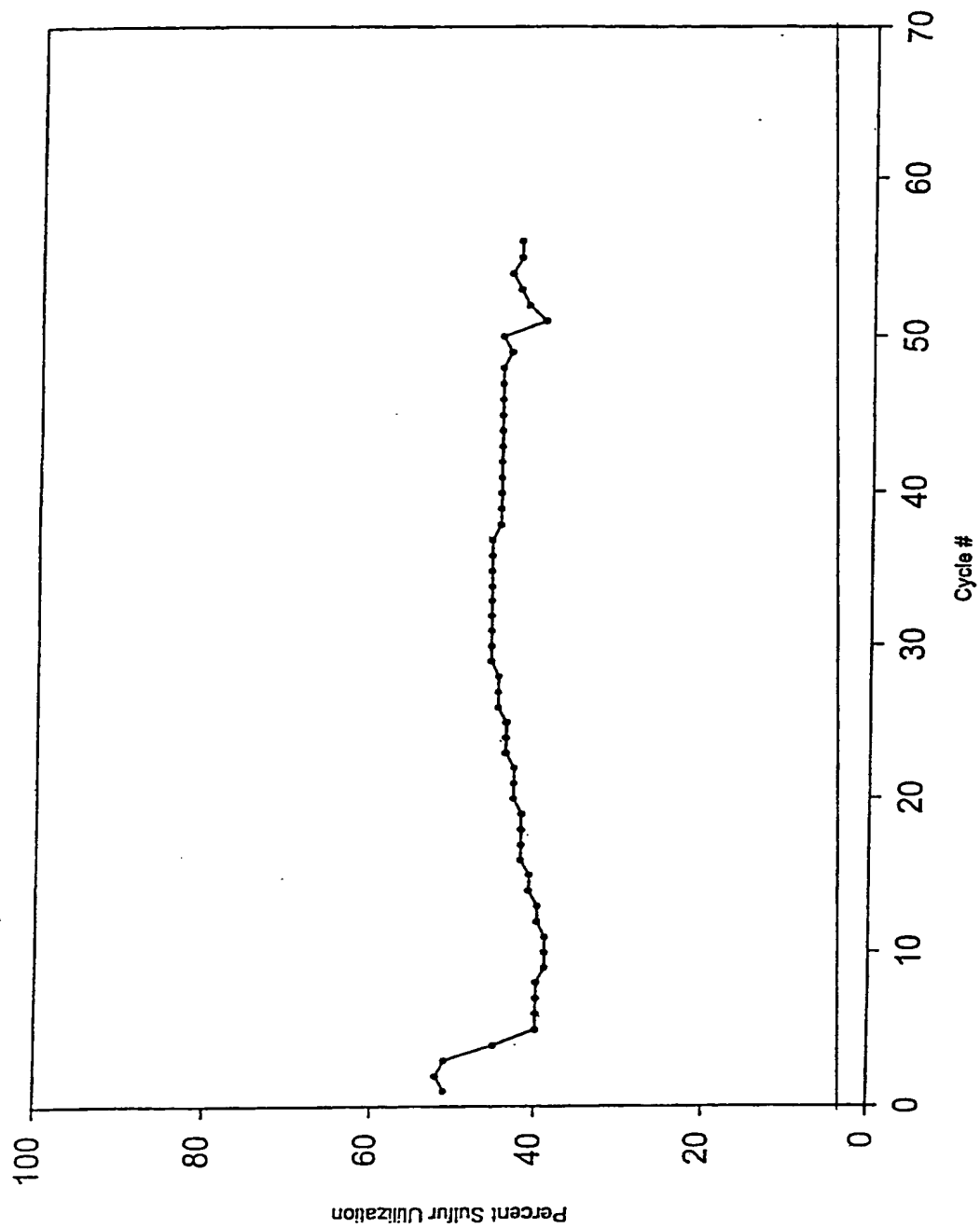
Percent Sulfur Utilization vs. number of recharge cycles (25°C)
Figure 10



Percent Sulfur Utilization vs. number of recharge cycles (25°C)

Figure 11

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Percent Sulfur Utilization vs. number of recharge cycles (25°C)

Figure 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/02909

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01M 4/58, 6/16

US CL :429/105

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/105, 325, 328, 329, 338, 339

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST (Derwent)

search terms: sulfide, sulphide, solvent, dissolve\$, cathod\$, catholyte

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,806,369 A (DEY et al) 23 April 1974, col. 3, lines 13-23, col. 4, lines 55-56.	18-25
Y		26
Y	US 4,237,200 A (WEDDIGEN) 02 December 1980, col. 1, lines 10-14, col. 2, lines 25-29.	26
A	US 4,469,671 A (BENNETT et al) 04 September 1984, col. 5, lines 1-10.	1-27
A	US 4,917,974 A (DE JONGHE et al) 17 April 1990, col. 3, lines 43-68.	1-27
A	US 5,506,072 A (GRIFFIN et al) 09 April 1996, col. 2, lines 47-67.	1-27

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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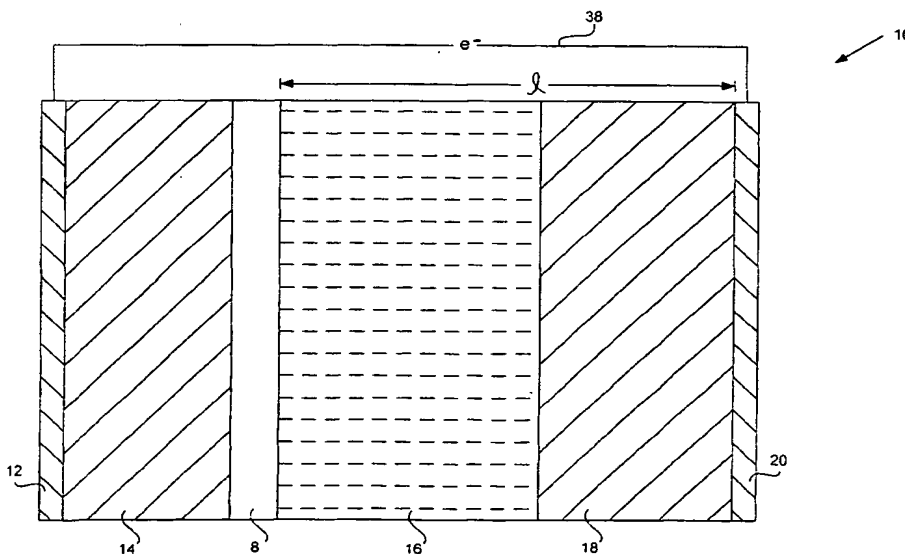
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[Continued on next page]

(54) Title: LIQUID ELECTROLYTE LITHIUM-SULFUR BATTERIES



(57) Abstract: A high performance lithium-sulfur battery cell (10) includes the following features: (a) a negative electrode (14) including a metal or an ion of the metal; (b) a positive electrode (18) comprising an electronically conductive material; and (c) a liquid catholyte (16) including a solvent and a dissolved electrochemically active material comprising sulfur in the form of a sulfide of the negative electrode metal or a polysulfide of the metal. Such battery cells are characterized by an energy density, calculated based upon a laminate weight, of at least 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². Cells meeting these criteria often find use as primary cells.

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LIQUID ELECTROLYTE LITHIUM-SULFUR BATTERIES

BACKGROUND OF THE INVENTION

This invention relates to metal-sulfur batteries (e.g., lithium-sulfur batteries).

5 The rapid proliferation of portable electronic devices in the international marketplace has led to a corresponding increase in the demand for advanced secondary batteries (i.e., rechargeable batteries). The miniaturization of such devices as, for example, cellular phones, laptop computers, etc., has naturally fueled the desire for rechargeable batteries having high specific energies (light weight). At the same
10 time, mounting concerns regarding the environmental impact of throwaway technologies, has caused a discernible shift away from primary batteries and towards rechargeable systems.

 In addition, heightened awareness concerning toxic waste has motivated, in part, efforts to replace toxic cadmium electrodes in nickel/cadmium batteries with the
15 more benign hydrogen storage electrodes in nickel/metal hydride cells. For the above reasons, there is a strong market potential for environmentally benign secondary battery technologies.

 Secondary batteries are in widespread use in modern society, particularly in applications where large amounts of energy are not required. However, it is desirable
20 to use batteries in applications requiring considerable power, and much effort has been expended in developing batteries suitable for high specific energy, medium power applications, such as, for electric vehicles and load leveling. Of course, such batteries would also be suitable for use in lower power applications such as cameras or portable recording devices. Primary batteries having specific energies and high power
25 densities also find use in many applications.

 Among the factors leading to the successful development of high specific energy batteries is the fundamental need for high cell voltage and low equivalent weight electrode materials. Electrode materials must also fulfill the basic electrochemical requirements of sufficient electronic and ionic conductivity, high
30 reversibility of the oxidation/reduction reaction, as well as excellent thermal and chemical stability within the temperature range for a particular application. Importantly, the electrode materials must be reasonably inexpensive, widely available, non-explosive, non-toxic, and easy to process.

Thus, a smaller, lighter, cheaper, non-toxic battery is sought for the next generation of batteries. The low equivalent weight of lithium renders it attractive as a battery electrode component for improving weight ratios. Lithium also provides greater energy per volume than do the traditional battery standards, nickel and cadmium.

The low equivalent weight and low cost of sulfur and its nontoxicity renders it also an attractive candidate battery component. Successful lithium/organosulfur battery cells are known. (See, De Jonghe et al., U.S. patent Nos. 4,833,048 and 4,917,974; and Visco et al., U.S. Patent No. 5,162,175.)

Recent developments in ambient-temperature sulfur electrode technology may provide commercially viable rechargeable lithium-sulfur batteries. Chu and colleagues are largely responsible for these developments which are described in the above-referenced U.S. Patent Nos. 5,582,623 and 5,523,179 (issued to Chu). These developments allow electrochemical utilization of elemental sulfur at levels of 50% and higher over multiple cycles. Because sulfur has a theoretical maximum capacity of 1675 mAh/g (assuming all sulfur atoms in an electrode are fully reduced during discharge), the utilization of sulfur in lithium-sulfur cells as described in the above Chu patents typically exceeds 800 milliamp-hours per gram (mAh/g) of sulfur. Chu's initial work focused on solid and gel-state batteries in which a solid or gel-state ionic conductor was immobilized with the sulfur in an electrode.

Prior to Chu's work, rechargeable ambient-temperature lithium-sulfur batteries were not considered commercially viable. The limited research that was conducted in the field almost universally employed liquid electrolytes which served not only as ionic transport media between the anode and cathode, but also as ionic conductors within the sulfur electrode. Without exception, these electrodes suffered from poor utilization of the sulfur electrode over repeated cycling. For example, one of the best reported rechargeable lithium-sulfur liquid electrolyte batteries cycled 120 times, but had a maximum sulfur utilization of only 5%. See Rauh, R.D., Pearson, G.F. and Brummer, S.B., "Rechargeability Studies of Ambient Temperature Lithium/Sulfur Batteries", 12TH IECEC, 283-287 (1977). Other rechargeable systems had higher sulfur utilizations, but unacceptably low cycle lives. For example, one group reports a maximum sulfur utilization of about 45%, but their cell was dead by 50 cycles and, during cycling, had a utilization of only about 25%. See Peled, E., Gorenshstein, A., Segal, M., Sternberg, Y., "Rechargeable Lithium-Sulfur Battery (Extended Abstract)", J. Power Sources, 26, 269-271, (1989). Because of their poor cycling performance, the vast majority of prior lithium-battery systems were at best deemed suitable only as

primary batteries. And even then, they were only functional at very low current densities. In addition, some researchers have concluded that liquid electrolyte/sulfur cells will be intrinsic limited to poor performance. See Coleman, J.R. and Bates, M.W., "The Sulfur Electrode", 289-302 (1968)

5 Other references to lithium-sulfur battery systems in liquid formats include the following: Yamin et al., "Lithium Sulfur Battery," J. Electrochem. Soc., 135(5): 1045 (May 1988); Yamin and Peled, "Electrochemistry of a Nonaqueous Lithium/Sulfur Cell," J. Power Sources, 9: 281 (1983); Peled et al., "Lithium-Sulfur Battery: Evaluation of Dioxolane-Based Electrolytes," J. Electrochem. Soc., 136(6): 1621
10 (June 1989); Bennett et al., U.S. Patent No. 4,469,761; Farrington and Roth, U.S. Patent No. 3,953,231; Nole and Moss, U.S. Patent No. 3,532,543; Lauck, H., U.S. Patent Nos. 3,915,743 and 3,907,591; Societe des Accumulateurs Fixes et de Traction, "Lithium-sulfur battery," Chem. Abstracts, 66: Abstract No. 111055d at page 10360 (1967); and Lauck, H. "Electric storage battery with negative lithium electrode and
15 positive sulfur electrode," Chem. Abstracts, 80: Abstract No. 9855 at pages 466-467 (1974).).

It now appears that the poor performance of the prior art lithium-sulfur cells resulted from various design flaws. For example, many cells employed large
20 reservoirs of liquid electrolyte in which sulfide and polysulfide discharge products dissolved, diffused away from the positive electrode, and became unavailable for further electrochemical reaction, thereby reducing the cell's capacity. In addition, it is likely that the prior art cells were operated under conditions in which their discharge products were irreversibly precipitated out of solution, thereby reducing capacity.

Still further, poor performance of the prior art cells may result from failure to
25 optimize the catholyte composition in conjunction with the cathode structure. Many prior art cathodes made use of traditional carbon structures including high surface area carbon and binder pressed into expanded metal. There are many disadvantages to such a design. First the pore structure of such cathodes limits the transport rate of dissolved sulfur species which leads to premature precipitation of sulfide discharge
30 products that leads to clogging of the positive electrode and then to cell polarization. Second, such cathodes may not have had an open pore structure, so that a significant part of the sulfur capacity is retained outside of the active area of the electrode.

What is needed therefore is a safe liquid electrolyte metal-sulfur battery system optimized for the chemical and electrochemical features of the sulfur rechargeable
35 electrode.

SUMMARY OF THE INVENTION

The present invention provides high performance thin film lithium-sulfur battery cells having liquid electrolytes. The cells preferably include the following features: (a) a negative electrode including a metal or an ion of the metal; (b) a positive electrode comprising an electronically conductive material; and (c) a liquid catholyte including a solvent and dissolved electrochemically active material comprising sulfur in the form of at least one of a sulfide of the metal and a polysulfide of the metal. Such battery cells are characterized by an energy density, calculated based upon a laminate weight, of at least about 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². Cells meeting these criteria often find use as primary cells.

In a preferred embodiment, the liquid catholyte has a sulfur concentration of at least about 6 M, more preferably at least about 7 M, and most preferably at least about 10 M. Preferably, the electrolyte solvent includes an ether such as dimethoxyethane. The electrolyte may include a cosolvent such as dioxolane. The electronically conductive material in the positive electrode may include at least one of carbon and an electronically conductive polymer. To ensure good utilization, the conductive material preferably comprises an interconnected matrix. In a primary cell, the positive electrode may be made relatively thick; e.g., having an average thickness of at least about 40 micrometers (not including the current collector).

Often the negative electrode is an alkali metal electrode such as a lithium metal electrode. Preferably, the negative electrode includes a protective layer that is conductive to ions of the metal and protects the electrode from attack by the electrolyte or sulfur.

Another aspect of the invention provides a rechargeable battery cell that may be characterized by the following features: (a) a negative electrode including a metal or an ion of the metal; (b) a positive electrode comprising a mixture of an electronically conductive material; and (c) a liquid catholyte including a solvent and dissolved electrochemically active material comprising sulfur in the form of at least one of a sulfide of the metal and a polysulfide of the metal. Such cell is further characterized by at least one of the following criteria: (i) the battery cell attains at least about 10% utilization over at least fifty cycles, and (ii) the battery cell attains at least about 50% utilization over two or more cycles. More stringent criteria include (iii) the battery cell attains at least about 30% utilization over at least 50 cycles or (iv)

the battery cell attains at least about 50% utilization over at least 10 cycles, or (v) the battery cell attains at least about 50% utilization over at least 75 cycles. Concerning discharge rate, the cell preferably discharges at an average current density of at least about 0.5 mA/cm² over at least 50 cycles in criteria (i) and at least 2 cycles in criteria
5 (ii). The positive electrode, negative electrode, and electrolyte preferably meet the criteria set out above for another aspect of the invention.

These and other features of the invention will be further described and exemplified in the drawings and detailed description below.

10

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a lithium/liquid electrolyte/sulfur cell of this invention.

Figure 2 is a process flow diagram of a preferred method for fabricating positive electrodes that may be employed in this invention.

15 Figure 3 is a table presenting various slurry compositions employed to fabricate sulfur electrodes for use in cells of this invention.

Figure 4 is a graph showing laminate power density versus laminate energy density for various primary cells constructed in accordance with this invention.

20 Figure 5 is a graph showing laminate power density versus laminate energy density for various secondary cells constructed in accordance with this invention.

Figure 6 is a table presenting the results of various experiments conducted in accordance with this invention.

Figure 7 is a graph of end of discharge voltage after each recharge cycle for the cell described in Example 1.

25 Figure 8 is a graph of the percent sulfur utilization after each recharge cycle for the cell described in Example 2.

Figure 9 is a graph of percent sulfur utilization versus cycle number for the cell described in Example 3.

30 Figure 10 is a graph of the percent sulfur utilization versus number of recharge cycles for the cell described in Example 4.

Figure 11 is a graph of percent sulfur utilization versus number or recharge cycles for the cell described in Example 5.

Figure 12 is a graph of percent sulfur utilization versus number or recharge cycles for the cell described in Example 6.

5

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

INTRODUCTION

This invention provides metal-sulfur batteries having low equivalent weight, high cell voltage and consequently a high specific energy, and operating at high sulfur utilization over many cycles. The batteries are preferably constructed in a thin film format such that the current density does not become diffusion limited. The invention also provides primary metal-sulfur cells having high specific energy.

In one embodiment, the battery cells of this invention include a liquid electrolyte solvent that contains one or more ethers. Preferably, the main electrolyte solvent includes a glyme or related compound. In a particularly preferred embodiment, the electrolyte includes dimethoxyethane (DME) and dioxolane.

The positive electrodes employed in batteries of this invention include a sulfur-based material having a relatively low equivalent weight. The electrodes, which may be composites, include in their theoretically fully charged state sulfur and an electronically conductive material. At some state of discharge, the positive electrode will include one or more of sulfides and polysulfides, which are sulfides and polysulfides of the metal or metals found in the negative electrode. In some embodiments, the fully charged electrode may also include some amount of such sulfides and/or polysulfides.

Sometimes the sulfur-based electroactive material in a positive electrode may be generally referred to as "active sulfur." As used herein, that term refers to electroactive material that is elemental sulfur or discharge products of elemental sulfur that would return to elemental sulfur in a theoretically fully charged state.

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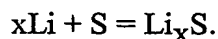
Upon discharge, the sulfur of the positive electrode reacts with the metal of the negative electrode to form the metal sulfides and polysulfides. For example, where M is the metal of the negative electrode, the overall cell reaction can be described as follows:



where M is any metal that can function as an active component in a negative electrode in a battery cell in which sulfur is the active component of the positive electrode; x = 0 through x = 2; z = the valence of the metal; and S is sulfur.

10 M is preferably at least one of an alkali metal, an alkaline earth metal, and a transition metals. M is more preferably selected an alkali metal, and still more preferably lithium or sodium. M is most preferably lithium.

In a preferred embodiment of this invention where the negative electrode contains lithium, the overall cell reaction wherein z = 1 can be described as follows:



15 When x = 2, 100% of the theoretical specific energy of the system has been released. If all elemental sulfur in the positive electrode reacts completely (so that all sulfur resides in Li₂S), the sulfur in the electrode is 100% utilized so that all 1675 mAh/g of sulfur is extracted during discharge.

20 From the above discussion, it should be apparent that upon discharge the positive electrode becomes a combination of sulfur, metal sulfides and polysulfides, and during the discharging process the proportions of those sulfur-containing components will change according to the state of charge. The charge/discharge process in the positive electrode is reversible. Similarly, upon recharging, the percentages of the sulfur-containing ingredient will vary during the process.

25 The positive electrode is fabricated such that it permits electrons to easily move between the sulfur and the electronically conductive material, and permits ions to move between the electrolyte and the sulfur. Thus, high sulfur utilization is realized after many cycles.

30 The present invention contemplates cell designs in which (1) all active sulfur is dissolved in electrolyte solution (one phase positive electrode) and (2) cell designs in which the active sulfur is distributed between a solid phase (sometimes precipitated) and a liquid phase. Each design has its advantages. The first design (all

sulfur is dissolved in the electrolyte) can be operated without producing precipitated active sulfur. Thus, there is less danger of the cell capacity being reduced due to unavailable precipitated electroactive species. The second design has a greater specific energy because the solid phase active sulfur contains a higher density of electroactive material. While the second design does have to contend with precipitated active sulfur and the possibility that electroactive species will be lost, certain design criteria can be employed to mitigate this potential detriment. For example, the cell can be configured or operated under conditions to minimize precipitation.

In a two phase design, the range of sulfur in such electrodes in the theoretically fully charged state is preferably from about 10% to 90% (more preferably 30% to 80%) by weight, excluding electrolyte. The sulfur-based composite electrode is preferably processed such that the component particles are homogeneously distributed, and segregation and/or agglomeration of the component particles is avoided.

A metal-sulfur battery system constructed with the sulfur-based positive electrode of this invention should have at least about 10%, and more preferably at least about 30%, availability of the sulfur, and most preferably at least about 50% availability of sulfur (during a single cycle). This availability corresponds to a minimum of 168 mAh/g (more preferably 504 mAh/g and most preferably 838 mAh/g) of sulfur included in the positive electrode. This is based on the above-mentioned theoretical value of 1675 mAh/gm of sulfur at 100% availability.

BATTERY DESIGN

Suitable batteries may be constructed according to the known art for assembling cell components and cells as desired, and any of the known configurations may be fabricated utilizing the invention. The exact structures will depend primarily upon the intended use of the battery unit. Examples include thin film with porous separator, thin film polymeric laminate, jelly roll (i.e., spirally wound), prismatic, coin cell, etc.

The negative electrode is spaced from the positive sulfur electrode, and both electrodes may be in material contact with an electrolyte separator. Current collectors contact both the positive and negative electrodes in a conventional manner and permit an electrical current to be drawn by an external circuit. In a typical cell, all of the

components will be enclosed in an appropriate casing, for example, plastic, with only the current collectors extending beyond the casing. Thereby, reactive elements, such as sodium or lithium in the negative electrode, as well as other cell elements are protected.

5 Conventional cell designs are known in the art, which may be consulted for details. Examples of sulfur cells employing various design configurations are set forth in the following references which are incorporated herein by reference for all purposes: (1) R.D. Rauh, F.S. Shuker, J.M. Marston and S.B. Brummer, *J. Inorg. Nuc. Chem.*, "Formation of Lithium Polysulfides in Aprotic Media", 39, 1761 (1977);
10 (2) R.D. Rauh, K.M. Abraham, G. F. Pearson, J.K. Suprenant and S.B. Brummer, "A Lithium/Dissolved Sulfur Battery with an Organic Electrolyte," *J. Electrochem. Soc.*, 126, 523 (1979); (3) H. Yamin, A. Gorenshtein, J. Penciner, Y. Sterberg, and E. Peled, "Lithium Sulfur Battery," *J. Electrochem. Soc.*, 135, 1045 (1988); (4) H. Yamin and E. Peled, "Electrochemistry of a Nonaqueous Lithium/Sulfur Cell," *J. Power*
15 *Sources*, 9, 281 (1983); and (5) E. Peled, Y. Sterberg, A. Gorenshtein, and Y. Lavi, "Lithium-Sulfur Battery: Evaluation of Dioxolane-Based Electrolyte," *J. Electrochem. Soc.*, 136, 1621 (1989).

Referring now to Figure 1, a cell 10 in accordance with a preferred embodiment of the present invention is shown. Cell 10 includes a negative current
20 collector 12, which is formed of an electronically conductive material. The current collector serves to conduct electrons between a cell terminal (not shown) and a negative electrode 14 (such as lithium) to which current collector 12 is affixed. If negative electrode 14 is made from lithium or other similarly reactive material, it will preferably include a protective layer 8 formed opposite current collector 12. Either
25 negative electrode 14 or protective layer 8 (if present) contacts a liquid electrolyte in an electrolyte region 16.

Region 16 may be delineated by the boundaries of a separator, which prevents electronic contact between the positive and negative electrodes. A positive electrode 18 abuts the side of separator layer 16 opposite negative electrode 14. As electrolyte
30 region 16 is an electronic insulator and ionic conductor, positive electrode 18 is ionically coupled to but electronically insulated from negative electrode 14. Finally, the side of positive electrode 18 opposite electrolyte region 16 is affixed to a positive current collector 20. Current collector 20 provides an electronic connection between a positive cell terminal (not shown) and positive electrode 18.

35 Current collectors 12 and 20, which provide current connections to the positive and negative electrodes, should resist degradation in the electrochemical environment

of the cell and should remain substantially unchanged during discharge and charge. In one embodiment, the current collectors are sheets of conductive material such as aluminum, copper, or stainless steel. The positive electrode may be attached to the current collector by directly forming on the current collector or by pressing a pre-formed electrode onto the current collector. Positive electrode mixtures formed directly onto current collectors preferably have good adhesion. Positive electrode films can also be cast or pressed onto expanded metal sheets. Alternately, metal leads can be attached to the positive electrode by crimp-sealing, metal spraying, sputtering or other techniques known to those skilled in the art. The sulfur-based positive electrode can be pressed together with the electrolyte separator sandwiched between the electrodes. In order to provide good electrical conductivity between the positive electrode and a metal container, an electronically conductive matrix of, for example, carbon or aluminum powders or fibers or metal mesh may be used.

In the case where sulfur is provided entirely as a dissolved species in the electrolyte, positive electrode 18 may primarily include an electronic conductor such as a carbon fiber matrix together with a binder or other additives. In the case where sulfur is provided in both the solid and liquid (dissolved) phases, positive electrode 18 will include some amount of active sulfur in conjunction with the electronic conductor and possibly additives.

The separator may occupy all or some part of electrolyte compartment 16. Preferably, it will be a highly porous/permeable material such as a felt, paper, or microporous plastic film. It should also resist attack by the electrolyte and other cell components under the potentials experienced within the cell. Examples of suitable separators include glass, plastic, ceramic, and porous membranes thereof among other separators known to those in the art. In one specific embodiment, the separator is Celgard 2300 or Celgard 2400 available from Hoechst Celanese of Dallas, Texas.

The separator may also be of the type sometimes referred to as a "polymer" separator membrane having a porous or microporous network for entraining liquid electrolyte. Such separators are described in US Patent No. 3,351,495 assigned to W. R. Grace & Co. and US Patent Nos. 5,460,904, 5,540,741, and 5,607,485 all assigned to Bellcore, for example. These patents are incorporated herein by reference for all purposes.

In a preferred embodiment, the metal-sulfur cell has relatively thick positive and negative electrodes. Such thick format cells are particularly beneficial for use as primary cells, although they are appropriate in some secondary cells as well. The additional material provided in the electrodes provides extra capacity for long life. In

a specific example, the positive electrode of a primary cell has an average thickness of at least about 40 micrometers and the positive electrode of a secondary cell has an average thickness of at most about 8 micrometers. These thicknesses apply to electrodes in which all sulfur is provided by the catholyte and those in which at least some sulfur is provided in the solid phase and localized at the electrode. Generally such thicknesses represent a bare minimum and are appropriate with very high concentration catholytes (e.g., 15 Molar sulfur or possibly even 25 Molar sulfur). In more typical embodiments, the positive electrode thickness will range between about 40 and 130 micrometers for primary cells and between about 8 and 30 micrometers for secondary cells. Note that it may be feasible and appropriate to provide sulfur as a suspension (e.g., a colloid) in the catholyte. Note also that it is generally desirable that the positive electrode have a relatively high porosity, possibly as high as 95% or more. Generally, higher porosity electrodes allow fabrication of cells with higher laminate energy densities because less electronic conductor is required. Of course, an electrode's porosity, capacity, and thickness are linked so that setting two of these parameters fixes the other.

ELECTROCHEMICAL AND CHEMICAL MECHANISMS OF LITHIUM-SULFUR LIQUID ELECTROLYTE BATTERIES

Referring again to Figure 1, lithium-sulfur cell 10 will be described with relevant reaction mechanisms explained. During normal charging, the electrons are extracted from positive electrode 18 and transported over electrical connection 38 to negative electrode 14. The removal of electrons at positive electrode 18 oxidizes the species present in the electrode. In this reaction, lithium ions are liberated from lithium sulfide and/or lithium polysulfide species present in the positive electrode. The species remaining in the positive electrode will have the general formula Li_2S_x , where x has a value of 1 or greater. Over time the charge reaction produces polysulfide species having longer and longer sulfur chains. It is known for example that in a normal charge reaction, the value of x in some polysulfides may be 12 or greater. In addition, some of the polysulfides will be further oxidized to elemental sulfur.

At the negative electrode, lithium ions present in the electrolyte 16 are transported through protective layer 8 and reduced to lithium metal as electrons are moved through electrical conduit 38.

The above electrode reactions proceed in the reverse direction during discharge. That is, the electrochemical reduction of active sulfur pulls electrons to positive electrode 18 through current collector 20 and from line 38. This reduces elemental sulfur, if present, to form various lithium species including lithium polysulfides and lithium sulfide. It also reduces the highly oxidized polysulfides to less oxidized polysulfides and lithium sulfide. Simultaneously, lithium ions are provided from negative electrode 14 through the electrolyte. The lithium ions are generated in conjunction with the flow of electrons from negative electrode 14 to line 38 (via current collector 12).

Generally, the higher molecular weight polysulfides (those with more sulfur atoms) are more highly soluble than their lower molecular weight counterparts. During discharge, these higher molecular weight species go into solution in the electrolyte and migrate throughout the cell. Some of the dissolved species move to the negative lithium metal electrode where they may be chemically reduced to form less-soluble lower molecular weight compounds such as lithium sulfide. Some of this lithium sulfide may beneficially act as a protective layer on the lithium metal electrode. However, lithium sulfide formed in excess of this beneficial amount may precipitate out a solution where it serves no beneficial use in the cell. In fact, this precipitated lithium sulfide (and/or less-soluble lower molecular weight polysulfides) represents lithium and sulfur that is no longer available for immediate participation in electrochemical reactions. Thus, precipitation of these compounds reduces the battery's capacity.

Precipitated sulfide or polysulfide may also form because the local solution concentration of these species exceeds their solubility limits. This occurs when the species are generated faster than they can diffuse away, a condition that exists when the local current density is too great in comparison with the mass transport rate. That is, the solution phase concentration gradient must support a mass flux that is sufficiently high to remove reaction products before they accumulate to their solubility limit. The present invention addresses this problem in at least two ways. First, it provides electrolyte solvents in which the discharge species are highly soluble and highly mobile thereby reducing the likelihood of precipitation. Second, it provides a cathode structure in which the mass flux is sufficiently fast that the local concentration of soluble species does not exceed the solubility limits.

Assuming that some precipitation will occur so that solid phase sulfur, sulfide, and/or polysulfide exist in the cell, it is important that the cell be designed to make these precipitated electroactive species available to electronic and ionic charge

carriers. This allows high utilization of the active sulfur in the cell. To this end, the electronic conductor in the positive electrode should form an interconnected matrix so that there is always a clear current path from the positive current collector to any position in the electronic conductor. The interconnected matrix of the electronic conductor should also be sufficiently "open" that there is room for precipitated electroactive species to deposit on the matrix. Finally, any binder employed in the positive electrode should not prevent contact between the electronic conductor and the electroactive species. For example, the binder should not provide so much wetting that precipitated sulfur particles and/or the current collector are completely wetted and therefore unable to exchange electrons.

LIQUID ELECTROLYTES

It has now been discovered that the performance of lithium-sulfur batteries can be improved by employing electrolyte compositions designed to solubilize lithium sulfide and relatively low molecular weight polysulfides. The new electrolytes of this invention are in fact designed to keep more sulfur discharge products in solution and therefore available for electrochemical reaction. In general, the electrolyte compositions of this invention include one or more solvents that strongly coordinate lithium. These solvents are "ionophores" for lithium ions. Exemplary ionophores are podands, coronands, and cryptands as described in chapter 10 of the treatise "Lithium Chemistry, A Theoretical and Experimental Overview," Anne-Marie Sapse and Paul Von Rague Schleyer, Eds. John Wiley & Sons, New York (1995) which is incorporated herein by reference for all purposes. Chapter 10 was written by Bartsch et al. Podands are acyclic multidentate ligands. Common examples are glymes and polyethylene glycols. Coronands are monocyclic multidentate ligands. Common examples are crown ethers and substituted crown ethers. Cryptands are multicyclic multidentate ligands.

In a preferred embodiment, the electrolyte solvents of this invention include one or more compounds having an ethanediether linkage. They have the general formula $R_1(CH_2CH_2O)_nR_2$, where n ranges between 1 and 10 and R_1 and R_2 are different or identical alkyl or alkoxy groups (including substituted alkyl or alkoxy groups). Alternatively, R_1 and R_2 may together form a closed ring to form a crown ether for example. Examples of linear solvents include the glymes $(CH_3O(CH_2CH_2O)_nCH_3)$ and related oxides of the formula $(CH_2CH_2O)_n(CH_2O)_p$, where p ranges from about 1 to 50. Such ethoxy repeating unit compounds serve as lithium ion coordinating solvents. In a preferred embodiment, the main solvent is a

glyme having a value of n ranging between 1 and 6. In an especially preferred embodiment, the glyme is dimethoxyethane ($\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3$).

5 The batteries of this invention can operate at room temperature. However, the present invention also pertains to systems operating at temperatures slightly outside of the ambient. Obviously, the choice of operating temperature ranges can influence the preferred electrolyte for the batteries of this invention. For example, at relatively low operating temperatures, lower molecular weight electrolytes will be preferred, so the value of " n " in the above-described ethanediether compounds will be in the lower end of the 1-10 range. At higher temperatures, the opposite is true.

10 While the electrolyte solvents described above are a main component of the electrolytes of this invention, one or more cosolvents may be provided with them. If such cosolvents are employed, they are preferably chosen to solubilize lithium cations or sulfide/polysulfide anions. In certain preferred embodiments, crown ethers and/or cryptands are provided as cosolvents. In other preferred embodiments, donor or
15 acceptor cosolvents may be employed. In a particularly preferred embodiment, the cosolvent is dioxolane. Preferred dioxolane-containing electrolytes are further described in US Patent Application No. 09/245,167, titled DIOXOLANE AS A COSOLVENT IN Li/Li₂S_x BATTERIES, filed on February 5, 1999, and having Nimon et al. as inventors. That document is incorporated herein by reference for all
20 purposes.

Crown ethers are macrocyclic polyethers generally having repeating ethoxy and/or propoxy groups. Crown ethers with 3 to 20 oxygen atoms have been synthesized. They are typically made up of linked ethoxy units $(\text{CH}_2\text{CH}_2\text{O})_n$ as shown below. A general abbreviation used is $n\text{-C-}m$ where n is the ring size and m is
25 the number of oxygen atoms in the ring.

Commercially available crown ethers which have application in this invention include 12-crown-4, 15-crown-5, 18-crown-6, and modified crowns such as dibenzo-18-crown-6. Crown ethers are known to be complexing agents which solubilize alkali metal cations in nonpolar solvents. 12-crown-4 is known to be specific for the lithium
30 cation.

In substituted crown ethers, one or more of the hydrogen atoms are replaced with a hydrocarbon group that may be linear, branched, or aromatic. These hydrocarbon groups may, in turn, be substituted with halo (F, Cl, Br, I), nitrile (CN), nitro (NO₂), hydroxy (OH), and other common substituent groups. Examples are
35 presented in chapter 10 of the above referenced "Lithium Chemistry" treatise.

Specific examples include dibenzo-14-crown-4, tetramethyl-12-crown-4, benzo-15-crown-5. Crown ethers may also be substituted with podand groups such as (-COCH₂CH₂OCH₃) to form podano-coronands or "lariat ethers."

In an alternative embodiment, the main solvent is a cryptand. Cryptands are also known to strongly complex with alkali metal cations. Structurally, they are similar to crown ethers but possess an additional (-XCH₂CH₂) bridge to create an additional ring. X may be an oxygen, nitrogen, or sulfur atom. Often X is nitrogen and the corresponding cryptands are described as containing two nitrogen atoms linked by three (CH₂CH₂O)_n bridges. These compounds are commonly identified by the number of oxygen atoms in each of the three bridges. Thus, a cryptand in which two of the bridges have n = 2 (two oxygen atoms) and a third bridge having n = 1 (one oxygen atom) is identified as [2.2.1]-cryptand.

One example of a general class of cosolvents is the donor solvents, which tend to solubilize cations and acceptor solvents which tend to solubilize anions. Donor solvents are characterized by high donor numbers DN. A desirable property of both donor and acceptor cosolvents used in this invention is a high dielectric constants, ϵ . Such solvents generally promote dissociation of an ionic solute or a contact ion-pair.

Generally, donor solvents are those solvents which can be characterized as Lewis bases (they may be aprotic solvents). Generally, these solvents are good at solvating cations such as lithium ions. Donor solvents promote the ionization of covalent compounds to form intimate (or contact) ion-pairs. The concept of a solvent donor number is further explained and exemplified in "Experimental Electrochemistry for Chemists," by Sawyer and Roberts, Jr., John Wiley & Sons, New York (1995). That reference is incorporated herein by reference for all purposes.

Suitable donor cosolvents include hexamethylphosphoramide, pyridine, N,N-diethylacetamide, N,N-diethylformamide, dimethylsulfoxide, tetramethylurea, N,N-dimethylacetamide, N,N-dimethylformamide, tributylphosphate, trimethylphosphate, N,N,N',N'-tetraethylsulfamide, tetramethylenediamine, tetramethylpropylenediamine, and pentamethyldiethylenetriamine. These assist in solvation of lithium ions.

Suitable acceptor solvents assist in solvation of the sulfide and polysulfide anions. Acceptor solvents are those solvents which can be characterized as Lewis acids (they may be protic or aprotic solvents) and promote solvation of anions. Examples include alcohols such as methanol, glycols such as ethylene glycol, and polyglycols such as polyethylene glycol, as well as nitromethane, trifluoroacetic acid, trifluoromethanesulfonic acid, sulfur dioxide, and boron trifluoride.

It should be understood that the electrolyte solvents of this invention may also include other cosolvents which do not necessary fall into the donor solvent and acceptor solvent classes. Examples of such additional cosolvents include sulfolane, dimethyl sulfone, dialkyl carbonates, tetrahydrofuran (THF), dioxolane, propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), butyrolactone, N-methylpyrrolidinone, dimethoxyethane (DME or glyme), and combinations of such liquids.

In general, the liquid electrolyte solvents of this invention include about 50 to 100% by weight of the main solvent (excluding salts) which is usually one or more podand such as the above-described ethanediether compounds. The balance will be one or more of the cosolvents listed above. More preferably, the electrolyte solvents include about 50 to 100% by weight main solvent, and most preferably between about 70 and 90% by weight main solvent. As noted, the main solvent is one or more of the lithium coordinating ionophores described above (podands such as glymes, coronands such as crown ethers, or cryptands). Aside from the main solvent, the electrolyte solvent may include one or more cosolvents (described above) which make up the balance. In a particularly preferred embodiment, the electrolyte solvent includes DME as the main solvent and dioxolane as the cosolvent, with the dioxolane making up between about 5 and 15% by volume of the mixture.

Exemplary but optional electrolyte salts for the battery cells incorporating the electrolyte solvents of this invention include, for example, lithium trifluoromethanesulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$), lithium triflate (LiCF_3SO_3), lithium perchlorate (LiClO_4), LiPF_6 , LiBF_4 , LiAsF_6 , as well as, corresponding salts depending on the choice of metal for the negative electrode, for example, the corresponding sodium salts. As indicated above, the electrolyte salt is optional for the battery cells of this invention, in that upon discharge of the battery, the metal sulfides or polysulfides formed can act as electrolyte salts, for example, $\text{M}_{x/z}\text{S}$ wherein $x = 0$ to 2 and z is the valence of the metal.

Regardless of whether the sulfur is present in a solid phase, the cells of this invention preferably operate with their electrolytes at a concentration of between about 3 and 30 molar sulfur, more preferably between about 5 and 25 molar sulfur, and most preferably between about 10 and 20 molar sulfur. The sulfur used in this measure is the sulfur atoms in electroactive species. Thus, for example, one molar Li_2S corresponds to one molar sulfur, whereas one molar Li_2S_5 corresponds to five molar sulfur, and one molar S_8 corresponds to eight molar sulfur. Note that in some

cases at least some of the sulfur may exist as a suspended particles within the catholyte.

It should be understood that some systems employing liquid electrolytes are commonly referred to as having "polymer" separator membranes. Such systems are considered liquid electrolyte systems within the context of this invention. The membrane separators employed in these systems actually serve to hold liquid electrolyte in small pores by capillary action. Essentially, a porous or microporous network provides a region for entraining liquid electrolyte. As mentioned above, such separators are described in US Patent No. 3,351,495 assigned to W. R. Grace & Co. and US Patent Nos. 5,460,904, 5,540,741, and 5,607,485 all assigned to Bellcore, for example.

POSITIVE ELECTRODE

The positive electrode must utilize an electrochemically active material capable of being reduced during discharge by reaction with metal ions from the negative electrode. In this invention, the electrochemically active material includes some substantial fraction of "sulfur." This does not mean that the positive electrode must rely exclusively upon sulfur for its electrochemical energy, but often this will be the case.

As mentioned, the electroactive sulfur in the positive electrode may be referred to as "active sulfur" which represents sulfur that is elemental or would be elemental in a theoretically fully charged state of the battery. The sulfur of the positive electrode may be defined another way: at least one of elemental sulfur, a sulfide of the metal from the negative electrodes, and a polysulfide of the metal from the negative electrode. These definitions capture positive electrodes in various states of charge. For example, even if the fully charged cell includes only elemental sulfur, a slightly discharged cell will have some of its elemental sulfur reduced to a metal polysulfide or metal sulfide. Further, the theoretically fully charged state of some cells of this invention need not require that the positive electrode be entirely converted to elemental sulfur. It may be possible in some cases to have the positive electrode be a highly oxidized form of lithium polysulfide, for example, as in Li_2S_x where x is five or greater. The fully charged positive electrode may also include a mixture of such polysulfides together with elemental sulfur and possibly even some sulfide. It should be understood that during charge, the positive electrode would generally not be of

uniform composition. That is, there will be some amount of sulfide, sulfur, and an assortment of polysulfides with various values of x.

Some or all of the active sulfur components may be dissolved in the electrolyte solvent. If the active sulfur is totally dissolved, then the solid phase structure of the positive electrode simply contains an electronic conductor and possibly some binder or other additive. The sulfur is provided by the solution for reaction at the positive electrode electronic conductor.

Solid phase sulfur positive electrodes of this invention preferably include an electronic conductor in intimate contact with the electrochemically active sulfur. The electrochemically active material must also be in intimate contact with an ion conductor. In the above referenced Chu patents, the ionic conductor typically was a separately added gel or solid state material present in the positive electrode. In the liquid electrolyte batteries of the present invention, the ionic conductor is preferably the electrolyte itself which permeates through the positive electrode and thereby remains in intimate contact with the sulfur (elemental sulfur, metal polysulfides, and/or metal sulfides).

Exemplary electronically conductive materials of the composite positive electrode include carbon black, graphite, carbon fibers, electronically conductive compounds with conjugated carbon-carbon and/or carbon-nitrogen double bonds, for example but not limited to, electronically conductive polymers, such as, polyaniline, polythiophene, polyacetylene, polypyrrole, and combinations of such electronically conductive materials. The electronically conductive materials of the positive electrode may also have electrocatalytic activity.

As mentioned above, the electronic conductor in the positive electrode preferably forms an interconnected matrix so that there is always a clear current path from the positive current collector to any position in the electronic conductor. This provides high availability of electroactive sites and maintained accessibility to charge carriers over repeated cycling. Often such electronic conductors will be fibrous materials such as a felt or paper. Examples of suitable materials include carbon papers from Lydall Technical Papers Corporation of Rochester, NH, graphite felts available from Electrosynthesis Company of Lancaster, NY, and carbon whiskers available from Applied Sciences Inc. Carbon whiskers have a very large aspect ratio. Whisker diameter is on the order of 100nm with a length of about 1um. They can be coated from a whisker containing slurry onto aluminum foil or impregnated or sprayed into a network structure such as carbon paper. In the case of whiskers spray coated

onto carbon paper, the whiskers adhere to the carbon fiber surface, creating a multi-porous highly conductive structure.

The sulfur is preferably uniformly dispersed in a composite matrix containing an electronically conductive material. Preferred weight ratios of sulfur to electronic conductor in the sulfur-based positive electrodes of this invention in a fully charged state are at most about 50:1, more preferably at most about 10:1, and most preferably at most about 5:1. The sulfur considered in these ratios includes both precipitated or solid phase sulfur as well as sulfur dissolved in the electrolyte. Preferably, the per weight ratio of electronic conductor to binder is at least about 1:1 and more preferably at least about 2:1.

The composite sulfur-based positive electrode may further optionally include performance enhancing additives such as binders, electrocatalysts (e.g., phthalocyanines, metallocenes, brilliant yellow (Reg. No. 3051-11-4 from Aldrich Catalog Handbook of Fine Chemicals; Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, Milwaukee, WI) among other electrocatalysts), surfactants, dispersants (for example, to improve the homogeneity of the electrode's ingredients), and protective layer forming additives to protect a lithium negative electrode (e.g.; organosulfur compounds, phosphates, iodides, iodine, metal sulfides, nitrides, and fluorides). Preferred binders (1) do not swell in the liquid electrolyte and (2) allow partial but not complete wetting of the sulfur by the liquid electrolyte. Examples of suitable binders include Kynar available from Elf Atochem of Philadelphia, PA, polytetrafluoroethylene dispersions, and polyethylene oxide (of about 900k molecular weight for example). Other additives include electroactive organodisulfide compounds employing a disulfide bond in the compound's backbone. Electrochemical energy is generated by reversibly breaking the disulfide bonds in the compound's backbone. During charge, the disulfide bonds are reformed. Examples of organodisulfide compounds suitable for use with this invention are presented in US Patents Nos. 4,833,048 and 4,917,974 issued to DeJonghe et al. and US Patent No. 5,162,175 issued to Visco et al.

METHODS OF MAKING A POSITIVE ELECTRODE

As mentioned, an important feature of this invention is the ability to provide electrodes having electroactive material (usually sulfur) in intimate contact with an electronic conductor. This facilitates electron transport to and from the active material to allow nearly complete utilization of the active material. Note that good utilization

also requires that ions be readily available to the sulfur. This criterion is met by ensuring that, during operation, any solid sulfur in the positive electrode is in intimate contact with the liquid electrolyte (which provides a necessary ionically conductive medium). Thus, the positive electrode should be made sufficiently permeable to the liquid electrolyte that most all the sulfur contacts electrolyte. If the sulfur is present only in the dissolved state (as catholyte), then the positive electrode is simply the electronically conductive material and possibly some binder and other additives. Such positive electrode should provide good contact with the catholyte to ensure rapid charge transfer between the solid and liquid phases.

Some relevant details of processes for fabricating positive electrodes suitable for use with this invention are provided in US Patent No. 5,582,623 (previously incorporated herein by reference). Much discussion in that application focused on three-part positive electrodes, which include a gel or solid-state ionic conductor in addition to the sulfur and electronic conductor. The positive electrodes used with the present invention rely on the electrolyte itself as the ionic conductor, and therefore do not require a separate ionic conductor. Nevertheless, the fabrication details provided in the '623 patent are generally applicable to the electrodes employed in the present invention.

One process for making positive sulfur-based electrodes suitable for use with this invention is outlined in the flow chart of Figure 2. A process 300 begins at 302 and then, in a step 304, a slurry is prepared from a liquid and at least some of the positive electrode components. The solid components of the slurry may include active sulfur, an electronic conductor, a dispersing agent, and a binder. After the slurry is formed, it is coated onto a substrate such as a current collector or carbon paper electronic conductor matrix. See step 306. At this point, the slurry liquid may be removed by any number of processes including evaporation. The resulting "preformed positive electrode" may then be treated at a step 308 according to a post coating process such as heating to bind the various solid phase electrode components. At the conclusion of step 308, a completed electrode has been produced. Then, at a step 310, the completed electrode is assembled into a battery cell, with the process being complete at 312.

During process 300, sulfur may be introduced into the positive electrode at various points as indicated by optional steps 350, 352, and 354. The sulfur may be introduced in at least one of these steps. At step 350, sulfur is optionally introduced as one of the solid components to the slurry prepared at step 304. Introduction of sulfur at step 350 is referred to as a "Type I" process. At step 352, sulfur may be

introduced during electrode treatment step 308. This is referred to herein as a "Type II" process and typically involves providing a concentrated solution of elemental sulfur, polysulfide, sulfide, or combination thereof to the preformed electrode. Finally, at step 354, sulfur may be introduced to the electrode during cell assembly (step 310) in a "Type III" process. In this case, the sulfur (as elemental sulfur, polysulfide, sulfide, or combination thereof) is provided in a concentrated electrolyte solution or suspension. It is important to recognize that the sulfur may be added to the electrode at any or more of steps 350, 352, and 354.

In slurry preparation step 304, the procedure should produce a uniform slurry, in which the solids are dispersed, stabilized and de-agglomerized. Details of a particular slurry preparation depends on the type and weight percents of the solids content as well as the type and amount of liquid solvent employed. There are, however, some general procedures that are typical for many of the slurry preparations.

A slurry typically includes solids dispersed and/or dissolved in a liquid phase. Solid slurry components may include an electronically conductive material, a binding agent, a dispersing agent, a solid state and/or gel state ionic conductor, and active sulfur (if any). Typically the solids content in the slurry is uniformly dispersed throughout the liquid phases, but some, all, or none of the solids may be dissolved in the liquid phases.

In a first method of slurry preparation, the active sulfur (if any), the electronically conductive material, and a dispersing agent are stir-mixed in an appropriate solvent until a uniform dispersion is formed. In a preferred embodiment, a dispersing agent is not added to the slurry as it provides no function in the final product and merely adds weight. The ratio of milliliters of solvent to grams of solid material depends on the desired composition and texture of the slurry. Some ranges for the liquids and solids weight percents are presented in the Table shown in Figure 3. Once the dispersion is uniformly mixed, the binding agent is gradually added to the dispersion in a step wise fashion while the dispersion is continuously stir-mixed. The gradual addition of the binding agent combined with continuous stir mixing of the dispersion helps to prevent flocculation and the creation of grossly large aggregates. The slurry is made uniform by stir mixing for a period of at least 24 hours followed by placing the slurry through a three roll mill.

In a second method of slurry preparation, the active sulfur (if any), the electronically conductive material and the dispersing agent are stir mixed in an appropriate solvent until the dispersion is uniform. This dispersion is known as dispersion #1. In a preferred embodiment, the dispersing agent is not added to the

slurry. The binding agent is added to an appropriate solvent in order to make a second dispersion, known as dispersion #2. Dispersion #2 is also stir mixed until it becomes uniform. Dispersion #2 is then slowly added to dispersion #1 while Dispersion #1 undergoes continuous stir-mixing. The slurry is stir mixed for 24 hours and then put
5 through a three roll mill to make it more uniform.

Representative electronically conductive materials used in the slurry include carbon blacks, graphites, carbon fibers and whiskers, electronically conductive compounds with conjugated carbon-carbon and/or carbon-nitrogen double bonds, for example but not limited to electronically conductive polymers, such as polyaniline, polythiophene, polyacetylene, polypyrrole, and combinations of such electronically
10 conductive materials. The electronically conductive material in the slurry provides a mechanism for electron transfer and for electronic conduction throughout the positive electrode. The weight percent of electronically conductive material in the solids content of the slurry typically ranges from 15%-85%, but can be as high a 100%.

Representative binding materials that in part comprise the slurry include but are not limited to polymeric materials, such as polyethylene oxide, polyvinylidene fluoride, polyethylene, polytetrafluoroethylene, electronically conductive polymers, such as polyaniline, polythiophene, polyacetylene, polypyrrole, and combinations of
15 such polymeric materials. The binder may be added to the slurry to enhance dispersion of the solids in the slurry and/or to stabilize the solids in the slurry from segregation, aggregation and/or flocculation. The binder may also be added to enhance the mechanical integrity of the positive electrode, to improve mechanical and electrical contact at the solid-solid interface and/or the solid/liquid interface, to
20 increase electronic and/or ionic conduction throughout the composite positive electrode, and still further, to enhance the electrochemical redox reactions. The solids content weight percent of binding materials in the slurry typically ranges from 5%-50%, but can be as low as zero percent.

Representative dispersing agents that in part comprise the slurry include but are not limited to low molecular weight polyethylene glycols, soya lecithin, etc., and
30 such dispersing agents that are well recognized in the field. The solids content weight percent of dispersing agent in the slurry can be as high as 25% and as low as zero percent, but is typically 2%-10%.

Active sulfur may also be added to the slurry, and this type of sulfur loading is known as type I sulfur loading. The active sulfur added to the slurry includes but is
35 not limited to elemental sulfur, sulfides, polysulfides, redox sulfur polymers, and a combination of such sulfur-containing materials.

Liquid phases are typically added to the slurry and can act as vehicles to better disperse, de-agglomerate and or dissolve the solids content. Typical liquid phases include but are not limited to acetonitrile, iso-propyl alcohol, tetrahydrofuran, carbon disulfide, tetraglyme, dibutyl phthalate and acetone.

5 Cathodes may be coated from the slurry (at step 306) using several variations of a Mayer rod method or using spray coating or other suitable method. In order to make uniform, crack free coatings that remain adhered to the current collector, special attention must be given to the coating process, especially when trying to formulate thicker cathode coatings on a flat sheet current collector. The following methods have
10 been found acceptable.

Method #1 -- This method is used for thin film coatings on a metallic current collector foil such as Al or stainless steel. A slurry is Mayer rod coated directly onto a metal current collector and the solvent is allowed to evaporate off. The thickness of the coating is controlled by the type of Mayer rod employed, the consistency of the
15 slurry, and the number of Mayer rod passes. For example, a coating thickness of 25 micrometers may be formed with a single pass of a Mayer rod having a wire diameter of 0.078 inches.

Method #2 -- This method is used for thicker film coatings on a metallic current collector foil such as Al or stainless steel. Method #2 is similar to that
20 described in Method #1, with the main difference being that the coatings are made with Mayer rods that have a pre-defined gap between the Mayer rod and the substrate. In a preferred embodiment, this gap ranges between about 0 and 200 micrometers.

Method #3 -- This method is used for impregnating slurry into carbon paper networks and carbon felt materials. In this method the slurry is vacuum impregnated
25 into a carbon paper. The carbon paper is placed on top of a silk screen that is molded to a vacuum plate. Slurry is impregnated into the carbon paper by Mayer rod coating while applying a vacuum to the backside of the carbon paper. The vacuum helps to load the slurry into the paper and allows for a more uniform distribution of slurry through the thickness of the paper. The amount of slurry inserted into the carbon
30 paper depends on the mesh size of the silk screen, the Mayer rod #, the viscosity of the slurry, and, of course, on the number of Mayer rod passes.

As mentioned, in Type II processes, active sulfur is introduced to the electrode during treatment step 308. After the slurry has been coated and dried, either on a flat metal sheet current collector or into a carbon paper network, it is considered a
35 preformed cathode. Preformed cathodes can be treated to a variety of different

procedures such as heat treatments, chemical treatments, etc. Possible chemical treatments serve to load additives and/or active sulfur to the cathode. One method for adding active sulfur to the cathode is to dissolve elemental sulfur in an appropriate highly volatile solvent and then to re-crystallize the sulfur on the surface of the preformed cathode. Of course, the active sulfur may remain in solution for liquid format batteries.

There are certain advantages of loading sulfur into a preformed cathode in this manner. For example, the electronically conductive network can be formed and optimized such that during sulfur dissolution the electronically conductive network does not break apart under the associated stresses.

The final cell assembly (step 310) may be performed in various manners. One part of the final cell assembly is to insert electrolyte into the cathode structure. If the electrolyte contains dissolved active sulfur, the sulfur loaded during this step is considered to be Type III sulfur loading. Care must be taken that the electrolyte remains within the confines of the cathode. Too much liquid in the battery cell can lead to a detrimental loss of active sulfur away from the carbon electrode. On the other hand, enough electrolyte must be added to the cathode to allow for a continuous pathway for the dissolved sulfur species to move away and then back to the redox sites in the cathode. Moreover, care must be taken to make sure that there is an adequate ionic pathway through the cathode, through the separator, and to the surface of the anode. The method used to insert the electrolyte into the cathode will depend strongly on the pore structure of the cathode and on the volatility of the liquid electrolyte. In general, the less volatile is the electrolyte, the more readily the electrolyte can be loaded into the cathode. On the other hand, volatile solvents typically have lower viscosity and as such may penetrate the cathode pore structure more effectively. The catholyte may be vacuum impregnated into the positive electrode as follows. First, place the catholyte on the electrode. Then, pull a vacuum under the electrode for several minutes. Finally, remove the vacuum.

While the above described process has been described in terms of batchwise steps, it will be apparent to those of skill in the art that many steps of the process may also be performed in a continuous fashion as described in the above-referenced US Patent No. 5,582,623.

NEGATIVE ELECTRODE

Most generally, the negative electrode can comprise any metal, any mixture of metals, glass, carbon or metal/carbon material capable of functioning as a negative electrode in combination with the sulfur-based composite positive electrode of this invention. Accordingly, negative electrodes comprising any of the alkali or alkaline earth metals or transition metals (the polyether electrolytes are known to transport divalent ions such as Zn^{++}), for example, in combination with the positive electrodes and electrolytes of this invention are within the ambit of the invention, and particularly alloys containing lithium and/or sodium.

Stated another way, the negative electrodes employed in the batteries of this invention may include a metal (in elemental or alloy form) or an ion of that metal as used in, for example, a carbon intercalation electrode or a glass matrix electrode. As explained above, metal ions from this negative electrode combine with elemental sulfur or polysulfides to produce a sulfide and polysulfides of the metal during discharge of the battery. Some of the resulting metal sulfides and polysulfides may remain localized near the positive electrode. Some fraction of these discharge products, however, will dissolve in the solvent of the electrolyte and move freely through the liquid containing regions of the cell. As mentioned, some of these dissolved discharge products may actually precipitate from solution and become unavailable for further electrochemical reaction, thereby reducing the cell's capacity. The present invention addresses this problem.

In one preferred embodiment, the materials for the negative electrodes include a metal such lithium or sodium or an alloy of one of these with one or more additional alkali metals and/or alkaline earth metals. Preferred alloys include lithium aluminum alloys, lithium silicon alloys, lithium tin alloys, and sodium lead alloys (e.g., Na_4Pb). Other metallic electrodes may include alkaline earth electrodes such as magnesium and their alloys; transition metal electrodes such as aluminum, zinc, and lead and their alloys;

The surface of such metallic negative electrodes can be modified to include a protective layer on the electrolyte side. This protective layer should be conductive to lithium ions and help prevent the formation of lithium dendrites or "mossy" lithium on repeated cycling. It can be produced by the action of additives, including organosulfur compounds, phosphates, iodides, nitrides, and fluorides. The protective layer may also be pre-formed from an inert physical barrier conductive to the metal ions from the negative electrode. Examples of such pre-formed protective layers include lithium phosphate, silicate glasses, polymers, or a combinations of these. In a particularly

preferred embodiment, the protective layer is poly(1-trimethylsilyl-1-propyne) ("PTMSP"). The protected negative electrodes may not require an electrolyte separator, thereby allowing the thin film cells of this invention to be made even thinner.

5 Examples of preferred protective layer formats and materials are described in the following US Patent applications, each of which is incorporated herein by reference for all purposes: US Patent Application No. 09/086,665, filed May 29, 1998, titled PROTECTIVE COATINGS FOR NEGATIVE ELECTRODES, and naming Visco et al. as inventors; US Patent Application No. 09/139,603, filed August
10 25, 1998, titled PLATING METAL NEGATIVE ELECTRODES UNDER PROTECTIVE COATINGS, and naming Chu et al. as inventors; US Patent Application No. 09/139,601, filed August 25, 1998, titled METHOD FOR FORMING ENCAPSULATED LITHIUM ELECTRODES HAVING GLASS PROTECTIVE LAYERS, and naming Visco et al. as inventors; and US Patent Application No.
15 09/431,190, filed November 1, 1999, titled ENCAPSULATED LITHIUM ALLOY ELECTRODES HAVING BARRIER LAYERS, and naming Chu et al. as inventors.

 In an alternative embodiment, the negative electrode may be an intercalation electrode such as a carbon-based lithium ion electrode. Such electrodes are available in commercial lithium ion batteries available from Sony Corporation of Japan. These
20 materials are described by Jeffrey Dahn in Chapter 1 of "Lithium Batteries, New Materials, Developments and Perspectives," edited by G. Pistoia and published by Elsevier (1994), which reference is incorporated herein by reference. Generally, such electrodes have the formula Li_yC_6 (where $y = 0.3$ to 2). For many of these materials, the fully charged electrode has the formula LiC_6 . The intercalation electrode matrix
25 may include graphite, petroleum coke, carbon inserted within highly disordered carbons, etc. The inserted carbon may also be doped with boron, phosphorus, or other appropriate dopant. In one example, the carbon may be prepared from low temperature pyrolysis (about 750°C) of carbon or carbon-silicon containing polymers such that the carbon product retains some hydrogen or silicon or both. (See, Sato et
30 al., "A Mechanism of Lithium Storage in Disordered Carbons," Science, 264: 556 (22 April 1994), which discusses very good results with a preferred negative electrode of Li inserted within poly p-phenylene-based carbon).

 Glass matrix negative electrodes such as $\text{Li}/\text{Sn}_2\text{O}_3$ and Li/SiO_2 may also be employed in the batteries of the present invention. These electrodes are similar to the
35 above-described carbon-based intercalation electrodes in that lithium ions are inserted therein during charge and removed during discharge. Such glass matrix electrodes are

described in various references including Tahara et al., European Patent Application No. 93111938.2 (1993), Idota et al. Canadian Patent Application, 21134053 (1994), and I. Courtney et al. Meeting Abstracts of the Electrochemical Society, Fall Meeting, San Antonio, TX, Oct. 6-11, 1996 Vol. 96-2, Abstract # 66, page 88, each of which is
5 incorporated herein by reference for all purposes.

UTILIZATION AND PERFORMANCE

In many cases, the battery cells of this invention are rechargeable or secondary cells. Unlike primary cells which discharge only once, the secondary cells of this
10 invention cycle between discharge and charge at least two times. Typically, secondary cells of this invention will cycle at least 50 times, with each cycle having a sulfur utilization (measured as a fraction of 1675 mAh/g sulfur output during the discharge phase of the cycle) of at least about 10%. More preferably, at least 50 cycles will have a minimum sulfur utilization of at least about 20% (most preferably at least about
15 30%). Alternatively, the secondary cells of this invention will cycle at least two times, with each cycle attaining at least 50% utilization of sulfur in the positive electrode.

As used herein, "utilization" assumes that if all elemental sulfur in an electrode is fully utilized, the electrode will produce 1675 mAh/g of sulfur. That is, 100% utilization corresponds to 1675 mAh/g of the sulfur in the cell, and 10% utilization
20 corresponds to 167.5 mAh/g of sulfur in the cell.

As illustrated in the examples below, the technology described herein enables metal-sulfur cells to perform at levels unachievable in the prior art. In addition to the high utilization and long cycle life described above, cells of this invention may exhibit very high energy and power densities. Preferably, high energy density is attained
25 while allowing discharge at relatively high, commercially useful, rates. In a preferred embodiment, metal-sulfur cells have a laminate energy density of at least about 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². More preferably, the metal-sulfur cells have a laminate energy density of at least about 450 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm². Following the
30 teachings of this invention, it is possible to fabricate cells having both the high laminate energy densities mentioned and laminate power densities in the region of 500 Watts/kilogram or higher. Such cells often find use as primary batteries.

Note that a "laminate" energy density is calculated by dividing the total energy obtained from the cell in a single cycle by the combined mass of the anode, cathode,

electrolyte and separator. The masses of the cell casing and any current collectors are not considered in the laminate energy density calculation. The "laminate power density" is obtained by dividing the total power obtained from the cell in a single cycle by the combined mass of the anode, cathode, electrolyte and separator. Again, the masses of the cell casing and any current collectors are not considered. The power density of a cell can be controlled by the rate of discharge. A higher rate of discharge generally provides a higher power density.

In a further preferred embodiment, the metal-sulfur cells have a laminate power density of at least about 200 Watts/kilogram, while maintaining a laminate energy density of at least about 40 Watt-hours/kilogram. Again, such cells often find use as primary batteries.

Regarding secondary metal-sulfur cells of this invention, they preferably maintain, over 10 more cycles, laminate power densities of at least about 10 Watts/kilogram and laminate energy densities of at least about 20 Watt-hours/kilogram. More preferably these laminate power and energies are maintained for at least about 100 cycles. The examples below show that metal-sulfur cells of this invention can maintain, over 10 or more cycles, laminate power densities of at about 40 Watts/kilogram in conjunction with laminate energy densities of at least about 50 Watt-hours/kilogram.

As mentioned, one of the benefits of using the electrolytes of this invention with lithium-sulfur cells is that they keep relatively insoluble sulfide and polysulfide discharge products in "circulation." The cathode constructions of this invention also serve the same purpose. This allows the capacity of the cell to remain high after repeated cycles.

It should be understood that using the electrolytes of this invention which solubilize sulfur discharge products to a great extent, "self-discharge" must be considered. That is, because the discharge products of the positive electrode are quite soluble in the electrolytes of this invention, they will automatically dissolve from the positive electrode and move to the negative electrode where they could be reduced chemically without producing electrical energy. Obviously, such self-discharged mechanism is to be avoided. One way of mitigating this effect is by providing a protective layer on the negative electrode which prevents these dissolved discharge products from reaching the negative electrode and thereby reacting with it. As mentioned above, such protective layers will generally conduct metal ions but not allow most other species from reaching the negative electrode. Again, examples of

protective layers include lithium phosphate, silicate glasses, polymers, or combinations of these.

EXAMPLES

5 The first 29 examples described herein are separated into 2 general types: primary and secondary. There are 19 primary examples and 10 secondary examples. The primary examples are differentiated between High Rate (HR) and High Energy Density (HED) examples. There are 3 High Rate examples (HR#1, HR#2, and HR#3), and there are 16 High Energy Density examples (HED #1, HED#2, etc). The
10 secondary examples are designated with "Cyc", for cycling. There are 10 secondary examples (Cyc #1, Cyc #2, etc).

Each example corresponds to a specific cathode (CAT-TY#), catholyte (C-LYTE-TY#) and cell type (CELL-TY#). Furthermore, each cathode type corresponds to a specific slurry type (SLY-TY#). A detailed description for each type follows.

15

Slurry

SLY-TY1 - The solids included ~70 wt% carbon black, ~25 wt% PEO (polyethylene oxide Mw=900K), and ~5 wt% Brij35. The solvent was acetonitrile. The solid content was approximately 6 % solids by total weight of slurry.

20 In a first 2 liter container, 45 grams of carbon black, 3.25 grams of Brij35 and 800ml of acetonitrile were stir-mixed, using a shearing blade, until a uniform dispersion was formed. In a second container, 16.25 grams of PEO were dissolved in 500ml of acetonitrile. The contents of the second container, dissolved PEO in acetonitrile, were gradually added to the first container while the first container was
25 continuously mixed with a shear blade. The slurry was then stir-mixed for approximately 4 hours and appeared uniform. Thereafter, the slurry was further homogenized by 3-roller milling.

SLY-TY2 - The solids included ~70 wt% carbon black and ~30 wt% PVdF (polyvinylidene flouride Mw~250,000). The solvent was Dimethyl formamide (DMF). The solid content was approximately 2 % solids by total weight of slurry.
30

3.5 grams of PVdF was stir-mixed, using a shearing blade, with 600ml DMF in a 800ml glass container until PVdF was totally dissolved in DMF. Thereafter, 8.2

grams of carbon black was added and the slurry was kept stirring for approximately 1.5 hours until the slurry appeared well mixed and uniform. Thereafter, the slurry was further homogenized using a Waring Commercial Blender.

5 SLY-TY3 - The solids included ~50% sulfur, ~28 wt% carbon black, ~20 wt% PEO (polyethylene oxide Mw=900K), and ~2 wt% Brij35. The solvent was acetonitrile. The solid content was approximately 11 % solids by total weight of slurry.

10 In a first 2 liter container, 42.67 grams of sublime sulfur, 23.90 grams of carbon black, and 400ml of acetonitrile were stir-mixed, using a shearing blade, until a uniform dispersion was formed. In a second container, 1.71 grams of Brij35 and 17.07 grams of PEO were dissolved in 400ml of acetonitrile. The contents of the second container, dissolved PEO and Brij35 in acetonitrile, were gradually added to the first container while the first container was continuously mixed with a shear blade. The slurry was then stir-mixed for approximately 4 hours and appeared uniform. Thereafter, the slurry was further homogenized by 3-roller milling.

15 SLY-TY4 - The solids included ~70 wt% carbon black, ~25 wt% PEO (polyethylene oxide Mw=900K), and ~5 wt% Brij35. The solvent was deionized water. The solid content was approximately 6 % solids by total weight of slurry.

20 The preparation process is similar to the one described in *SLY-TY1* except the slurry was milled using a colloid mill.

 SLY-TY5 - The solid content materials were ~70 wt% carbon whiskers, ~25 wt% PVdF (polyvinylidene fluoride Mw~250,000), and ~5 wt% Brij35. The solvent was solvent was dimethyl formamide (DMF). The solid content was approximately 7 % solids by total weight of slurry.

25 In a first container, 1.4 grams of Brij35 and 350 ml of DMF were stir-mixed, using a shearing blade. Thereafter, 19.5 grams of carbon whiskers was added to the first container. The contents in the first container were stir-mixed for about 20 minutes and then placed in a blender for 15 minutes, until the whiskers appeared wetted and paste-like. The contents of the first container were then 3-roller milled. A second container having 7 grams of PVDF dissolved in 50ml of DMF, was added to the first container and stir-mixed for 3 hours. Thereafter the slurry was 3 roller milled.

Cathode Coating Methods

Method #1: Doctor blade coating

In this method, slurry was coated directly on a 25 μ m-thick Al foil substrate using a wireless Mayer-rod as doctor blade. Thickness of the coating was controlled by a pre-defined gap between the wireless Mayer-rod and the Al foil substrate.

5 *Method #2: Air Spraying*

Spray coating was performed with an airbrush. Network substrates such as carbon paper or Al foil substrates were coated by spray coating.

Method #3: Vacuum Impregnation

10 Vacuum impregnation method was used to coat carbon paper substrates. The carbon paper was placed on top of a silk screen that was molded to a vacuum plate. The slurry was impregnated into the carbon paper by Mayer rod coating while applying a vacuum to the backside of the carbon paper. The amount of slurry inserted into the carbon paper depended on the mesh size of the silk screen, the Mayer rod size number, the viscosity of the slurry, and the number of Mayer rod passes.

15

Cathode Description

CAT-TY1 - CAT-TY1 is a carbon paper type cathode loaded with carbonaceous slurry. It was prepared by coating method #3 using slurry SLY-TY1. Coating thickness was about 210 μ m with a weight of 3.4 mg/cm².

20 CAT-TY2 - CAT-TY2 is a carbon paper type cathode loaded with carbonaceous slurry. It was prepared by coating method #2 using slurry SLY-TY2. Coating thickness depends on slurry weight; see Table 2.

Table 2

Slurry weight (mg/cm ²)	Cathode weight (mg/cm ²)	Cathode thickness (μ m)
0.3	1.56	250
0.6	1.86	250

1.4	2.66	300
-----	------	-----

CAT-TY3 - CAT-TY3 is a carbon paper type cathode loaded with a carbonaceous-sulfur slurry. It was prepared by coating method #3 using slurry SLY-TY3. Coating thickness and sulfur loading depends on slurry weight; see Table 3.

5

Table 3

Slurry weight (mg/cm ²)	Cathode weight (mg/cm ²)	Cathode thickness (μm)	Theoretical mAh/cm ²
10.6	11.86	340	9
14.0	15.26	390	12
17.7	18.96	500	15

CAT-TY4 - CAT-TY4 is a carbonaceous cathode coated on aluminum foil. It was prepared by coating method #1 using slurry SLY-TY4. Coatings with three different thicknesses have been prepared; see Table 4.

10

Table 4

Slurry weight (mg/cm ²)	Cathode weight (mg/cm ²)	Cathode thickness (μm)
0.5	7.06	32
1.2	7.76	44
1.9	8.46	54

CAT-TY5 - This cathode is similar to CAT-TY3 except that a thicker carbon paper was employed. Typical cathode weight was 7.9mg/cm². Cathode thickness was about 350um.

5 CAT-TY6 - CAT-TY6 is a fibril carbonaceous cathode coated on aluminum foil. It was prepared by coating method #2 using slurry SLY-TY5. Typical cathode weight was 13mg/cm². Cathode thickness was about 250um.

Cell Description

10 CELL-TY1 - CELL-TY1 is a laboratory cell that includes a cell laminate having a single anode layer, a single separator layer and a single cathode layer. The anode was 125um thick lithium from Cypress Foote Mineral Company; the cathodes were of type CAT-TY1, CAT-TY2, CAT-TY3, and CAT-TY4; the separator was Celgard 2400 obtained from Hoechst Celanese Company. The cell laminate was sandwiched between two stainless steel current collectors. The cells were loaded with
15 electrolyte or catholyte in an argon filled dry box, and final cell assembly, including sealing the cells was also performed in an argon filled dry box. The cell was removed from the dry box after sealing and testing on Maccor Battery Testers of the type Maccor model Series 4000.

20 CELL-TY2 - CELL-TY2 is a fully packaged battery having a pouch cell configuration in which the battery was sealed from the atmosphere by a polymeric laminate material such as PE/Al foil/PE. The contents of the cell were stacked and/or folded layers of a cell laminate that includes an anode, separator, and cathode, and sometimes additionally included a cathode current collector and an anode current collector. The anode was 125 micrometer lithium foil from Cypress Foote Mineral
25 Company; the cathodes were CAT-TY1, CAT-TY2, CAT-TY3, and CAT-TY5; the separator was Celgard 2400 from Celgard Company. The cell tabs, which extended to the outside of the battery pouch, were made of stainless steel, copper, aluminum, and/or nickel. Dry cells were assembled in a dry room. Cells were filled with electrolyte and/or catholyte in an argon filled dry box. After loading with electrolyte
30 or catholyte the cells were vacuum-sealed. Cell capacity depended on the number of stacked or folded layers and the composition of the cathode and catholyte.

Catholyte/Electrolyte Description

Electrolyte included organic solvent(s) and supporting salt. Catholyte included organic solvent(s), active sulfur and, in certain formulations, supporting salt.

Table 5

Category	Molarity Sulfur	Molarity LiDTF	Solvents
C-LYTE-TY1	2.5	0.25	DME/DIOX (90/10 vol%)
C-LYTE-TY2	3.4	0.34	DME/DIOX (90/10 vol%)
C-LYTE-TY3	5.7	0.38	DME/DIOX (90/10 vol%)
C-LYTE-TY4	7.5	0.5	DME/DIOX (90/10 vol%)
C-LYTE-TY5	8	0	DME/DIOX (90/10 vol%)
C-LYTE-TY6	10	0	DME/DIOX (90/10 vol%)
C-LYTE-TY7	12	0	DME/DIOX (90/10 vol%)
C-LYTE-TY8	3	0.5	Tetraglyme
C-LYTE-TY9	3	0.5	Tetraglyme/DME (50/50 vol%)
E-LYTE	0	0.5	DME/DIOX (90/10 vol%)
C-LYTE TY10	13.5	0	DME/DIOX (90/10 vol%)

Note that the carbon black (100% compressed acetylene black) used in these examples was manufactured by Chevron Chemical Co. The carbon whiskers were manufactured by Applied Sciences, Inc. The Cathode Network Matrixes CP-035 and CP-050 were manufactured by Lydall Tech. Papers. CP-035 had a fiber diameter of 10 micrometers, a weight of 1.26 mg/cm², a thickness of 210 micrometers and an open volume of 97%. CP-050 had a fiber diameter of 10 micrometers, a weight of 1.80 mg/cm², a thickness of 320 micrometers and an open volume of 97%.

Regarding the cathode components, the sublimed sulfur, the Li₂S, and the LiDTF were all manufactured by Aldrich corporation. The lithium used in the anodes was 125 micrometers thick and manufactured by Cypress Foote Mineral Company.

Regarding the solvents, the deionized water was manufactured by VWR, the acetonitrile was manufactured by Spectrum, and the DMF, DME, 1,3 dioxolane, and tetraglyme were all manufactured by Aldrich.

For the binders, the PVDF was Kynar 741 manufactured by Elf Atochem and had a molecular weight of 240,000 ~ 275,000 and the PEO was manufactured by Aldrich and had a molecular weight of 900,000. The polyethylene glycol dodecyl ether dispersion material was manufactured by Fluka.

Other cell components included the separator Celgard 2400 from Hoechst Celanese and the aluminum current collector (cathode) 25 micrometer thick 1100 alloy manufactured by All Foils of Brooklyn Heights, Ohio. The stainless steel 321 was likewise manufactured by All Foils.

Figures 4 and 5 show the laminate energy density and laminate power density for various cells constructed with the components and processes described above. As mentioned, the laminate energy and power densities are calculated by dividing the total energy or power obtained from the cell in a single cycle by the combined mass of only the anode, cathode, electrolyte and separator. In Figures 4 and 5, the various cells are identified by the alphanumeric identifiers that follow.

Room Temperature Primary Cells

HR #1

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY1*, tested at room temperature and at 10 mA/cm², yields 33 Wh/kg for the

battery, 55 Wh/kg for the laminate, 386 W/kg for the battery, and 655 W/kg for the laminate.

HR #2

- 5 Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY1*, tested at room temperature and at 20 mA/cm², yields 26 Wh/kg for the battery, 47 Wh/kg for the laminate, 747 W/kg for the battery, and 1320 W/kg for the laminate.

10 *HR #3*

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY1*, tested at room temperature and at 30 mA/cm², yields 26 Wh/kg for the battery, 49 Wh/kg for the laminate, 1056 W/kg for the battery, and 1849 W/kg for the laminate.

15

HED #1

Cell of type *CELL-TY2*, cathode of type *CAT-TY5*, 4.8 ml of catholyte type *C-LYTE-TY9*, tested at room temperature and at 0.1 mA/cm², yields 400 Wh/kg for the battery and 540 Wh/kg for the laminate.

20

HED #2

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 1.86 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY5*, tested at room temperature and at 1.0 mA/cm², yields 300 Wh/kg for the battery and 476 Wh/kg for the laminate.

25

HED #3

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY4*, tested at room temperature and at 1.0

mA/cm², yields 373 Wh/kg for the laminate.

HED #4

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
5 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 1.0
mA/cm², yields 445 Wh/kg for the laminate.

HED #5

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
10 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY7*, tested at room temperature and at 1.0
mA/cm², yields 384 Wh/kg for the laminate.

HED #6

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
15 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY4*, tested at room temperature and at 0.1
mA/cm², yields 373 Wh/kg for the laminate.

HED #7

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
20 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 0.1
mA/cm², yields 445 Wh/kg for the laminate.

HED #8

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.56
25 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY7*, tested at room temperature and at 0.1
mA/cm², yields 384 Wh/kg for the laminate.

HED #9

Cell of type *CELL-TY1*, cathode of type *CAT-TY3* with the weight of 11.86 mg/cm², 0.25 ml electrolyte of type *E-LYTE*, tested at room temperature and at 1.0 mA/cm², yields 281 Wh/kg for the laminate.

5

HED #10

Cell of type *CELL-TY1*, cathode of type *CAT-TY3* with the weight of 15.26 mg/cm², 0.25 ml of electrolyte type *E-LYTE*, tested at room temperature and at 1.0 mA/cm², yields 169 Wh/kg for the laminate.

10

HED #11

Cell of type *CELL-TY1*, cathode of type *CAT-TY3* with the weight of 18.96 mg/cm², 0.25 ml of electrolyte type *E-LYTE*, tested at room temperature and at 0.1 mA/cm², yields 136 Wh/kg for the laminate.

15

HED #12

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 0.35 ml of catholyte type *C-LYTE-TY10*, tested at room temperature and at 0.2 mA/cm², yields 517 Wh/kg for the laminate.

20

HED #13

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.86 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 2.0 mA/cm², yields 320 Wh/kg for the laminate.

25

HED #14

Cell of type *CELL-TY1*, cathode of type *CAT-TY2* with the weight of 1.86 mg/cm², 0.3 ml of catholyte type *C-LYTE-TY6*, tested at room temperature and at 3.0

mA/cm², yields 237 Wh/kg of the laminate.

HED #15

- 5 Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.2 ml of catholyte of type *C-LYTE-TY3*, tested at room temperature and at 5.0 mA/cm², yields 77 Wh/kg for the battery, 131 Wh/kg for the laminate, 204 W/kg for the battery, and 343 W/kg for the laminate.

HED #16

- 10 Cell of type *CELL-TY1*, cathode of type *CAT-TY6*, 0.37 ml of catholyte type *C-LYTE-TY4*, tested at room temperature and at 1.0 mA/cm², yields 295 Wh/kg for the laminate

Room Temperature Secondary Cells

- 15 *Cyc #1*

Cell of type *CELL-TY1*, cathode of type *CAT-TY4* with the weight of 7.06 mg/cm², 0.035 ml of catholyte type *C-LYTE-TY8*, cycled at room temperature and at 0.1 mA/cm² discharge / 0.1 mA/cm² charge, yields 500 cycles at 27 Wh/kg for the laminate.

20

Cyc #2

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 8.4 ml of catholyte type *C-LYTE-TY4*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge, yields 30 cycles at 155 Wh/kg for the battery and 203 Wh/kg for the laminate.

25

Cyc #3

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.2 ml of catholyte type *C-LYTE-TY4*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm²

charge, yields 20 cycles at 133 Wh/kg for the battery and 222 Wh/kg for the laminate.

Cyc #4

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY2*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge, yields 100 cycles at 76 Wh/kg for the battery and 130 Wh/kg for the laminate.

Cyc #5

Cell of type *CELL-TY2*, cathode of type *CAT-TY1*, 3.6 ml of catholyte type *C-LYTE-TY2*, cycled at room temperature and at 0.75 mA/cm² discharge / 0.25 mA/cm² charge with 0.74 mA/cm² discharge capacity cutoff, yields 430 cycles at 37 Wh/kg for the battery and 64 Wh/kg for the laminate.

Cyc #6

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY3*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge with 2.84 mA/cm² discharge capacity cutoff, yields 60 cycles at 90 Wh/kg for the battery and 156 Wh/kg for the laminate.

Cyc #7

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY3*, cycled at room temperature and at 1.0 mA/cm² discharge / 0.5 mA/cm² charge with 20% capacity cutoff, yields 150 cycles at 61 Wh/kg for the battery and 104 Wh/kg for the laminate.

Cyc #8

Cell of type *CELL-TY2*, cathode of type *CAT-TY2* with the weight of 2.66 mg/cm², 4.4 ml of catholyte type *C-LYTE-TY3*, cycled at room temperature and at 1.0

mA/cm² discharge / 0.5 mA/cm² charge, yields 4 cycles at 170 Wh/kg for the battery and 297 Wh/kg for the laminate.

Cyc #9

- 5 Cell of type *CELL-TY1*, cathode of type *CAT-TY4* with the weight of 7.76 mg/cm², 0.045 ml of catholyte type *C-LYTE-TY8*, cycled at room temperature and at 0.1 mA/cm² discharge / 0.1 mA/cm² charge, yields 300 cycles at 43 Wh/kg for the laminate.

10 *Cyc #10*

Cell of type *CELL-TY1*, cathode of type *CAT-TY4* with the weight of 8.46 mg/cm², 0.06 ml of catholyte type *C-LYTE-TY8*, cycled at room temperature and at 0.1 mA/cm² discharge / 0.1 mA/cm² charge, yields 100 cycles at 56 Wh/kg for the laminate.

15

- As shown in Figure 4, primary cells of this invention discharged at low to moderate discharge rates (relatively low power densities) have very large laminate energy densities. As illustrated, cells of this invention may also be discharged at high rates (associated with high laminate power densities) for high power applications.
- 20 Typically, such cells have a somewhat lower laminate energy density.

- As shown in Figure 5, secondary cells of this invention of this invention have good laminate energy densities and laminate power densities even after numerous cycles. While many discharge/charge cycles can degrade the performance of a cell, many cells constructed in accordance with this invention maintain very good
- 25 performance over hundreds of cycles as shown in Figure 5.

- Other experiments were conducted to demonstrate the performance advantages provided by the various aspects of this invention. The results of a few such experiments are tabulated in Figure 6. It should be understood that the experiments described herein represent but a small sampling of all experiments on lithium-sulfur
- 30 liquid systems conducted by or under the direction of the inventors. The experiments are provided mainly to show the high level of performance that can be attained when following the guidelines presented herein.

Example 1

A cathode film was made by mixing 50 (wt)% elemental sulfur, 24% carbon black, 18% polyethylene oxide Mw=900k (PEO), 2% Brij, and 6% lithium-trifluoromethanesulfonimide, in a solution of acetonitrile (solvent to solids ratio, 20:1 by weight). The components were stir-mixed for approximately two days until the slurry is well mixed and uniform. Thin cathode film were cast directly onto stainless steel current collectors, and the solvent was allowed to evaporate at ambient temperatures. The resulting cathode film weighed approximately 0.0015 gm per cm².

The separator was a micro-porous polymeric sheet having a nominal thickness of 1 mil (Hoechst Celanese, Celgard 2400). The cathode film and microporous separator were vacuum dried overnight to remove moisture prior to transfer into the argon glovebox for final cell assembly.

65 microliter of the electrolyte, which was a 0.5 molar solution of lithium-trifluoromethanesulfonimide (3M Company of Charlotte, North Carolina) in tetraglyme, was placed on the cathode film followed by placement of the microporous separator on the cathode. An additional 90 microliter of electrolyte was then placed on the micro-porous separator. A 5 mil (125 micron) thick high purity lithium anode film (FMC/Lithco of Gastonia, NC) was then placed on the other side of the microporous separator sheet.

The cell was then evaluated at 25°C with a Series 4000 battery test system from Maccor Inc. of Tulsa OK. This cell was cycled to a constant capacity corresponding to delivering 180 mAh per gm of the sulfur in the cell, that is, a utilization of 11% of the sulfur. The rates used were 90 microamp/cm² for discharging and 40 microamp/cm² for charging to cutoff voltages of 1.8 and 3.2 volts, respectively. Figure 7 shows the end of discharge voltage of this cell after each recharge cycle. As evident from the graph the cell performance is very consistent and over 600 cycles have been obtained.

Example 2

A cathode film was made by impregnating a slurry identical to the one described in example 1 into a carbon fiber paper (Lydall Technical Papers, Rochester, NY), and the solvent was allowed to evaporate at ambient temperatures. (This cathode was a carbon paper impregnated with slurry such that sulfur loading is of type I (see "methods" section)). The resulting cathode film weighed approximately 0.0029

gm per cm² and was vacuum dried overnight prior to transfer into the argon glovebox for final cell assembly.

135 microliter of the electrolyte of a 0.5 molar solution of lithium-trifluoromethanesulfonimide in tetraglyme was placed on the cathode film followed by placement of the microporous separator on the cathode. The separator was identical to the one described in example 1. An additional 45 microliter of electrolyte was then placed on the other side of the micro-porous separator. A 5 mil (125 micron) thick lithium anode film (FMC/Lithco Gastonia, NC) was then placed on the micro-porous separator sheet. Once assembled, the cell was compressed at 2 psi.

The cell was tested under similar conditions as described in example 1. The rates used were 90 microamp/cm² for discharging and for recharging. Figure 8 shows the percent sulfur utilization of this cell after each recharge cycle. As evident from the graph the cell performance is very consistent and more than 70 recharge cycles have been obtained at a sulfur utilization of approximately 40%.

Example 3

A cathode film similar to the one described in example 2 was made with a slurry composition of 70 (wt)% carbon black, 25% polyethylene oxide (PEO, Mw=900k) and 5% Brij. The resulting cathode film weighed approximately 0.0037 g/cm² and was vacuum dried overnight prior to transfer into the argon glovebox for final cell assembly. (This cathode was a carbon paper cathode impregnated with slurry; sulfur loading was of type III.)

Sulfur was added to the cathode by inserting 200 microliter of a tetraethylene glycol dimethyl ether solution containing 0.5 moles of lithium-trifluoromethanesulfonimide and approximately 3 moles of sulfur dissolved. After insertion of the dissolved sulfur into the cathode, the microporous separator (identical to the one described in example 1) was placed on the cathode. This was then followed by the placement of an additional 20 microliter of the above mentioned dissolved sulfur solution on the microporous separator. A 5 mil (125 micron) thick lithium anode film (FMC/Lithco Gastonia, NC) was then placed on the micro-porous separator sheet. Once assembled, the cell was compressed at 2 psi.

The cell was tested under similar conditions as described in example 1. The rates used were 500 microamp/cm² for discharging to a cutoff voltage of 1.5 V and 90 microamp/cm² for recharging. Figure 9 shows the percent sulfur utilization of this cell after each recharge cycle. As evident from the graph the cell performance is very

consistent and more than 70 recharge cycles have been obtained at a sulfur utilization of approximately 40%.

Example 4

5 A cell identical to the one in example 3 was tested under similar conditions as described in example 1 at a discharge rate of 90 microamp/cm². Figure 10 shows that the sulfur utilization of this cell is of approximately 60% for more than 35 recharge cycles.

Example 5

10 A cell similar to the one described in example 3, but having a cathode weight of 0.00197gm/cm² and 230 microliters of the dissolved sulfur solution (identical to the sulfur solution described in example 3) impregnated into the cathode, was tested under similar conditions as described in example 1. The rates used were 1000 microamp/cm² for discharging to a cutoff voltage of 1.5 V and 500 microamp/cm² for recharging. The total volume of catholyte added to the cell was 250 microliters. As
15 evident from Figure 11 the cell performance is very consistent and more than 30 recharge cycles have been obtained at a sulfur utilization of approximately 30%.

Example 6

A cathode film similar to the one described in example 3 was made with a slurry composition of 80 (wt)% carbon black, and 20% by solids content weight of a
20 teflon dispersion (DuPont Company of Wilmington, Delaware). (The cathode is similar to the one in example 3, except the cathode components are active sulfur, Teflon binder and carbon black, in this example there is no solid state ionic conductor or gelled ionic conductor. The sulfur loading is of Type III.) The resulting cathode film weighed approximately 0.0039 g/cm² and was vacuum dried overnight prior to
25 transfer into the argon glovebox for final cell assembly. The cell performance is shown in Figure 12.

OTHER EMBODIMENTS

30 The foregoing describes the instant invention and its presently preferred embodiments. Numerous modifications and variations in the practice of this invention are expected to occur to those skilled in the art. For example, the invention may provide overcharge protection as described in US Patent Application No.

08/686,609, filed July 26, 1996, and entitled RECHARGEABLE POSITIVE ELECTRODES and US Patent Application No. 08/782,245, filed March 19, 1997, and entitled OVERCHARGE PROTECTION SYSTEMS FOR RECHARGEABLE BATTERIES. Such modifications and variations are encompassed within the
5 following claims.

All references cited herein are incorporated by reference for all purposes.

CLAIMS*What is claimed is:*

1. A battery cell comprising:
 - a) a negative electrode including a metal or an ion of the metal;
 - b) a positive electrode comprising an electronically conductive material; and
 - c) a liquid catholyte including a solvent and dissolved electrochemically active material comprising sulfur in the form of at least one of a sulfide of the metal and a polysulfide of the metal, wherein the battery cell is characterized by an energy density, calculated based upon a laminate weight, of at least about 400 Watt-hours/kilogram when discharged at a rate of at least 0.1 mA/cm².
2. The battery cell of claim 1, wherein the battery cell is a primary battery cell.
3. The battery cell of claim 1, wherein the liquid catholyte has a sulfur concentration of at least about 5 M.
4. The battery cell of claim 1, wherein the liquid catholyte has a sulfur concentration of at least about 7 M.
5. The battery cell of claim 1, wherein the liquid catholyte has a sulfur concentration of at least about 10 M.
6. The battery cell of claim 1, wherein the battery cell attains at least about 10% utilization at ambient temperature.
7. The battery cell of claim 1, wherein the battery cell attains at least about 20% utilization at ambient temperature.
8. The battery cell of claim 1, wherein the positive electrode comprises a layer having an average thickness of at least about 40 micrometers.
9. The battery cell of claim 1, wherein the solvent comprises an ether.
10. The battery cell of claim 9, wherein the ether is dimethoxyethane.
11. The battery cell of claim 9, wherein the solvent further comprises dioxolane.
12. The battery cell of claim 1, wherein the solvent further comprises dioxolane.
13. The battery cell of claim 1, wherein the electronically conductive material comprises at least one of carbon and an electronically conductive polymer.

14. The battery cell of claim 1, wherein the electronically conductive material comprises an interconnected matrix.

5 15. The battery cell of claim 1, wherein the negative electrode is an alkali metal electrode.

16. The battery cell of claim 15, wherein the negative electrode is a lithium metal electrode.

10 17. The battery cell of claim 1, wherein the negative electrode includes a protective layer that is conductive to ions of the metal and protects the electrode from attack by the electrolyte.

15 18. A rechargeable battery cell comprising:
a) a negative electrode including a metal or an ion of the metal;
b) a positive electrode comprising a mixture of an electronically
conductive material; and
c) a liquid catholyte including a solvent and dissolved
20 electrochemically active material comprising sulfur in the form of at
least one of a sulfide of the metal and a polysulfide of the metal,
wherein the rechargeable battery cell is characterized by at least
one of the following criteria:
i) the battery cell attains at least about 10% utilization over at
25 least fifty cycles, and
ii) the battery cell attains at least about 50% utilization over two
or more cycles.

19. The battery cell of claim 18, wherein the battery cell attains at least about
30 30% utilization over at least fifty cycles.

20. The battery cell of claim 18, wherein the battery cell attains at least about
50% utilization over at least 10 cycles.

35 21. The battery cell of claim 18, wherein the battery cell attains at least about
50% utilization over at least 75 cycles.

22. The battery cell of claim 18, wherein the metal and a negative electrode is
at least one of sodium and lithium.

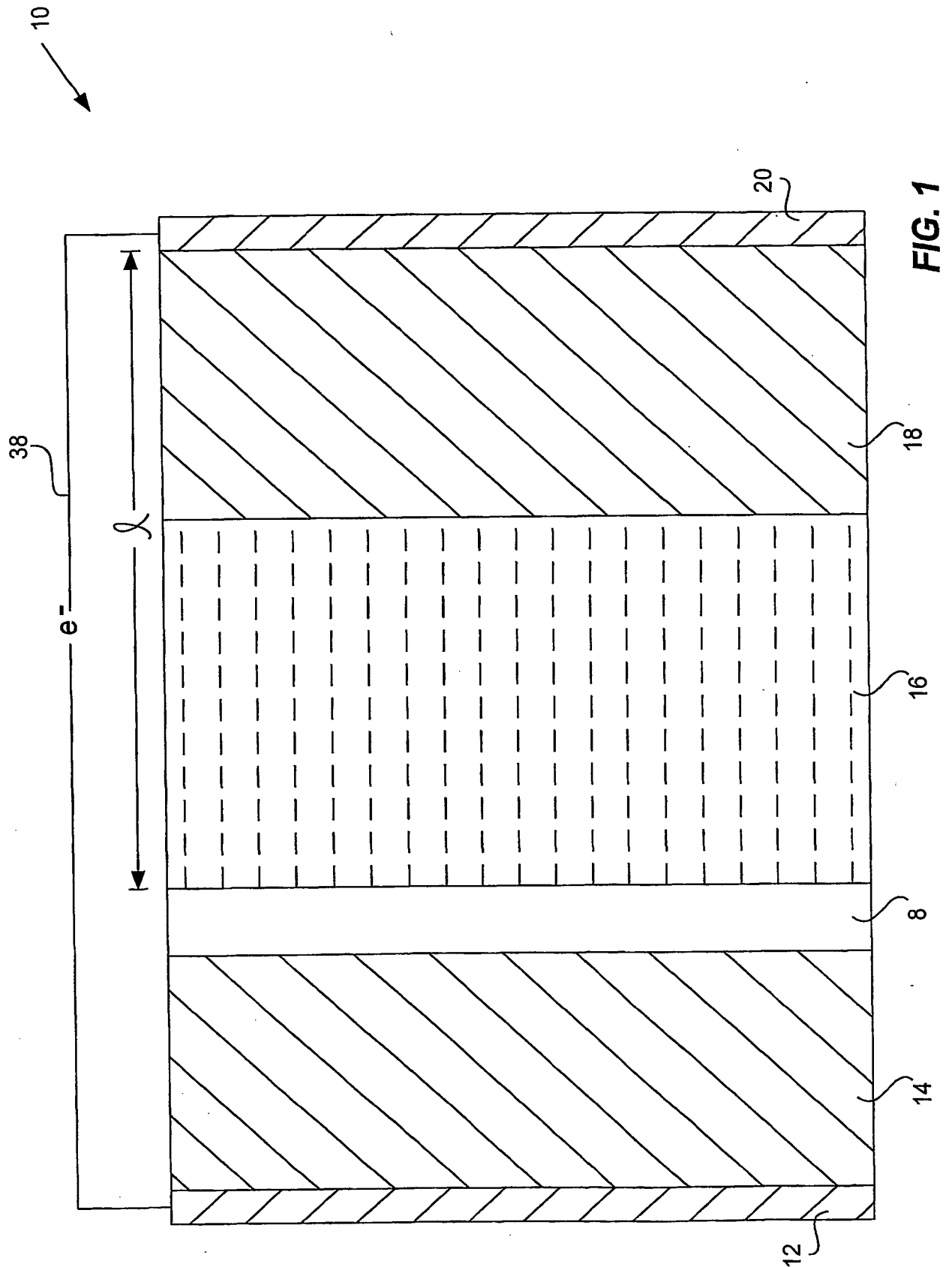
40 23. The battery cell of claim 18, wherein the negative electrode is a lithium
intercalation electrode.

24. The battery cell of claim 18, wherein the electronic conductor of the
45 positive electrode is at least one of carbon and an electronically conductive polymer.

25. The battery cell of claim 18, wherein the liquid electrolyte solvent includes
an ether.

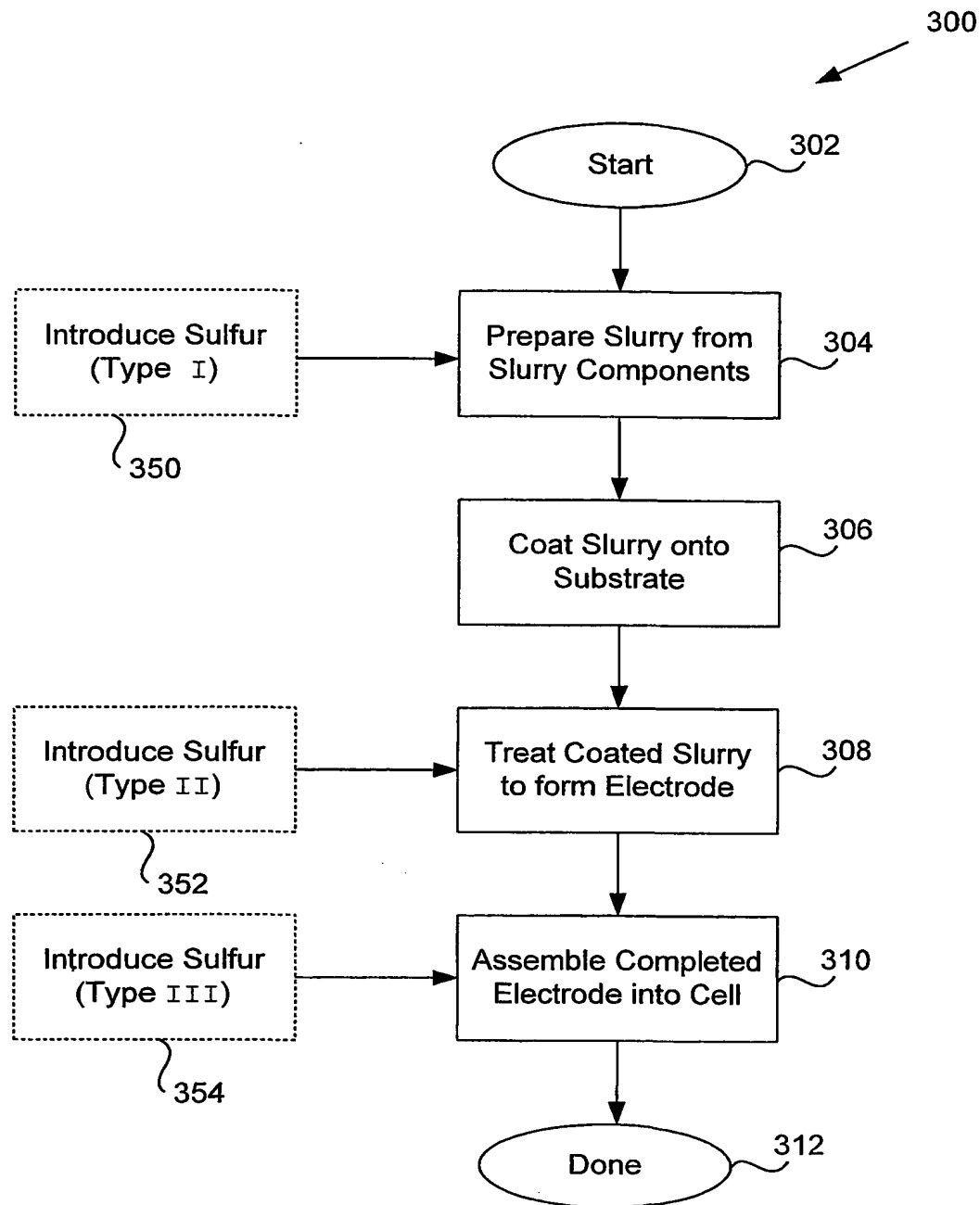
26. The battery cell of claim 18, wherein the electronically conductive material comprises an interconnected matrix.

27. The battery cell of claim 18, wherein the cell discharges at an average
5 current density of at least about 0.5 mA/cm^2 over at least 50 cycles in criteria (i) and at least 2 cycles in criteria (ii).



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**FIG. 2**

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	electronically conductive material	wt %	binding agent	wt %	dispersing agent	wt %	active sulfur	wt %	electrolyte salt	wt %	liquid solvent	wt ratio of liquids to solids
slurry #1	acetylene black (Chevron)	24%	PEO, Mw=900k (Aldrich)	20%	Brij 35 (Aldrich)	2%	elemental (sublimed from Aldrich)	50%	Li-tri- fluoromethane sulfonimide, (HW-115, 3M Company)	4%	Acetonitrile	50:1
slurry #2	acetylene black (Chevron)	10%	PEO, Mw=900k (Aldrich)	20%	Brij 35 (Aldrich)	5%	elemental (sublimed from Aldrich)	65%	none	NA	Acetonitrile	20:1
slurry #3	acetylene black (Chevron)	28%	PEO, Mw=900k (Aldrich)	20%	Brij 35 (Aldrich)	2%	elemental (sublimed from Aldrich)	50%	none	NA	Acetonitrile	20:1
slurry #4	acetylene black (Chevron)	70%	PEO, Mw=900k (Aldrich)	25%	Brij 35 (Aldrich)	5%	none	NA	none	NA	Acetonitrile	20:1
slurry #5	graphite flake (Asbury Graphite)	70%	PEO, Mw=900k (Aldrich)	25%	Brij 35 (Aldrich)	5%	none	NA	none	NA	Acetonitrile	20:1
slurry #6	XC-72 (Cabot)	70%	PEO, Mw=900k (Aldrich)	25%	Brij 35 (Aldrich)	5%	none	NA	none	NA	Acetonitrile	20:1
slurry #7	acetylene black (Chevron)	80%	Teflon (DuPont Company)	20%	none	NA	none	NA	none	NA	Isopropyl alcohol	30:1

FIG. 3

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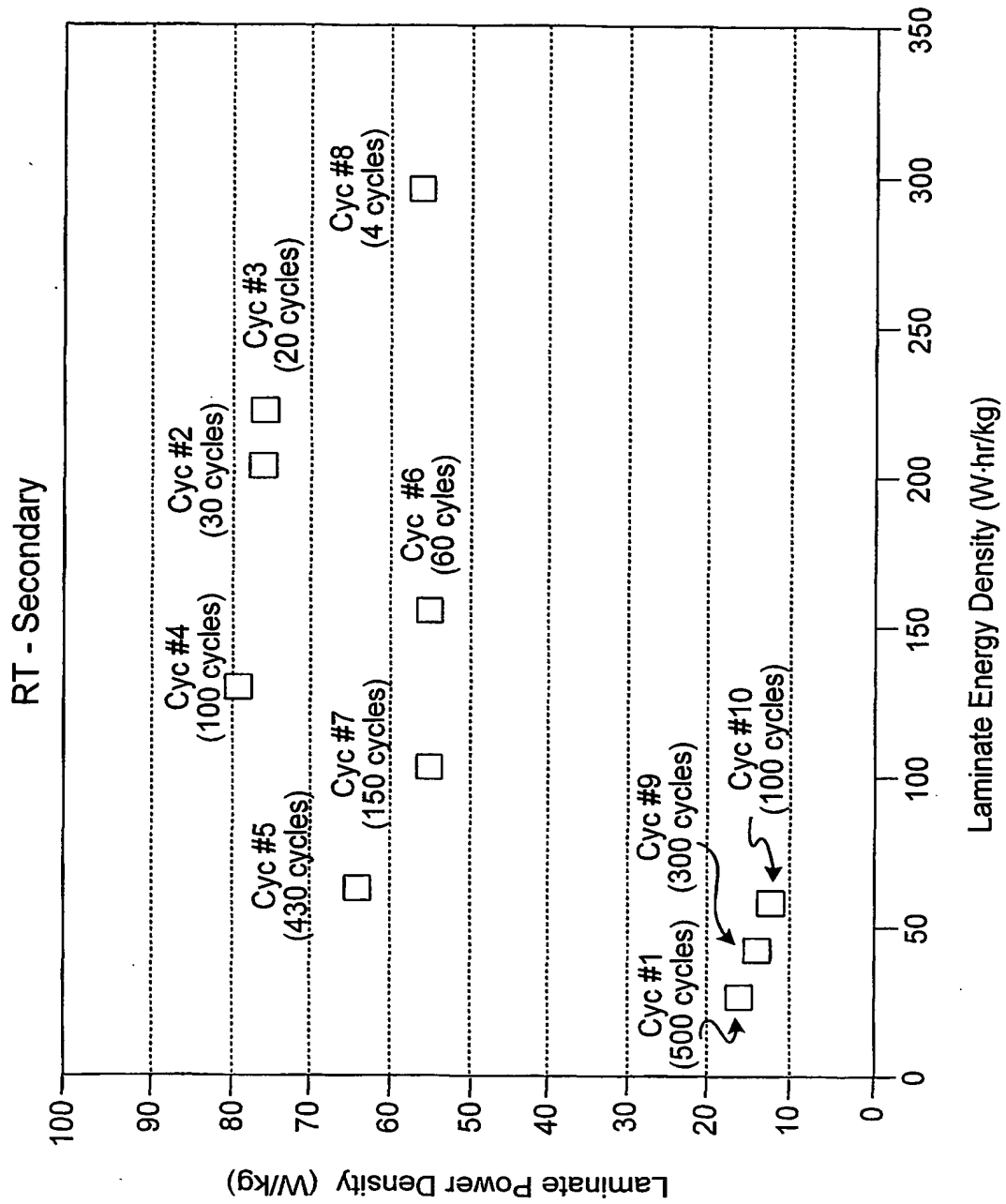


FIG. 4

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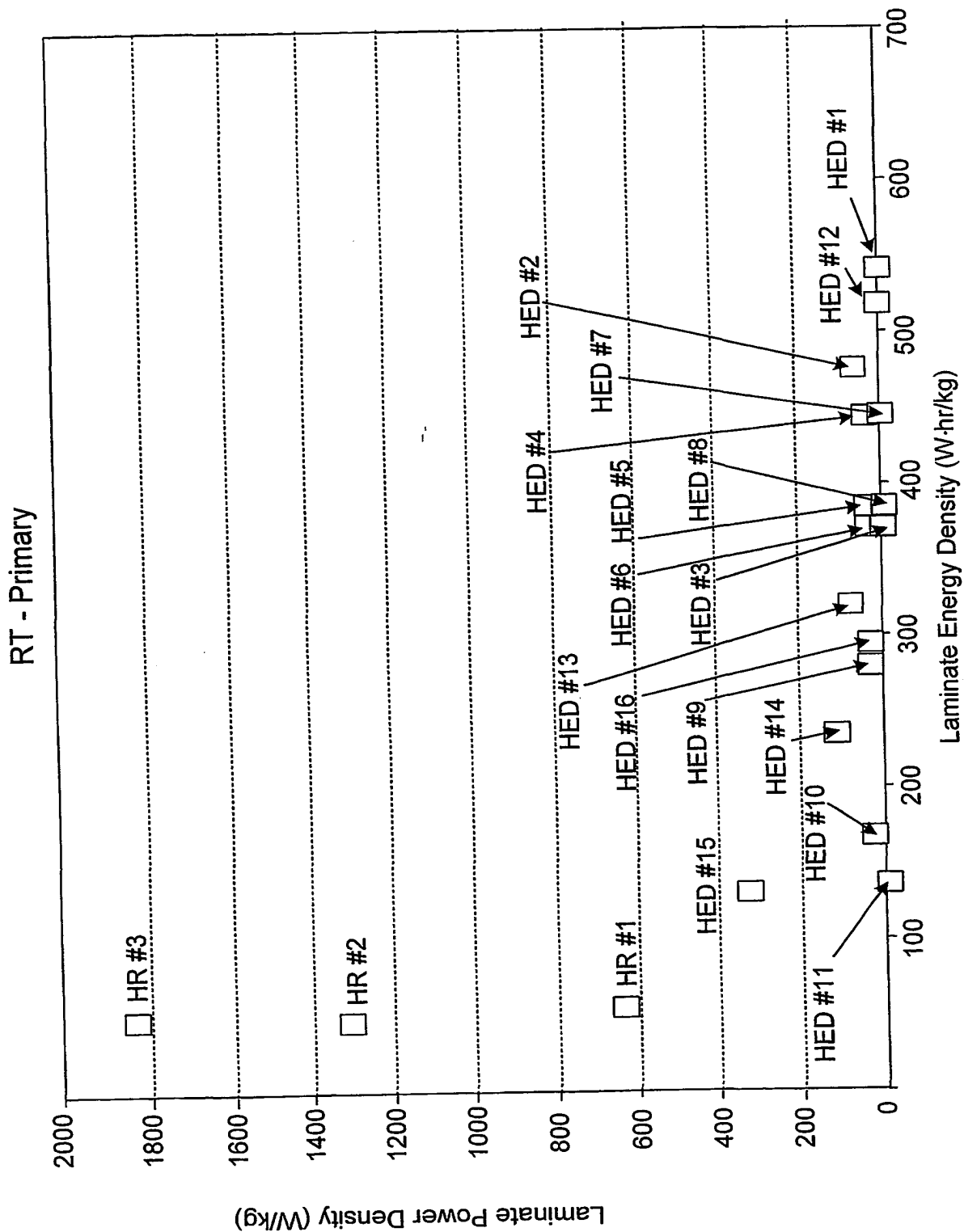


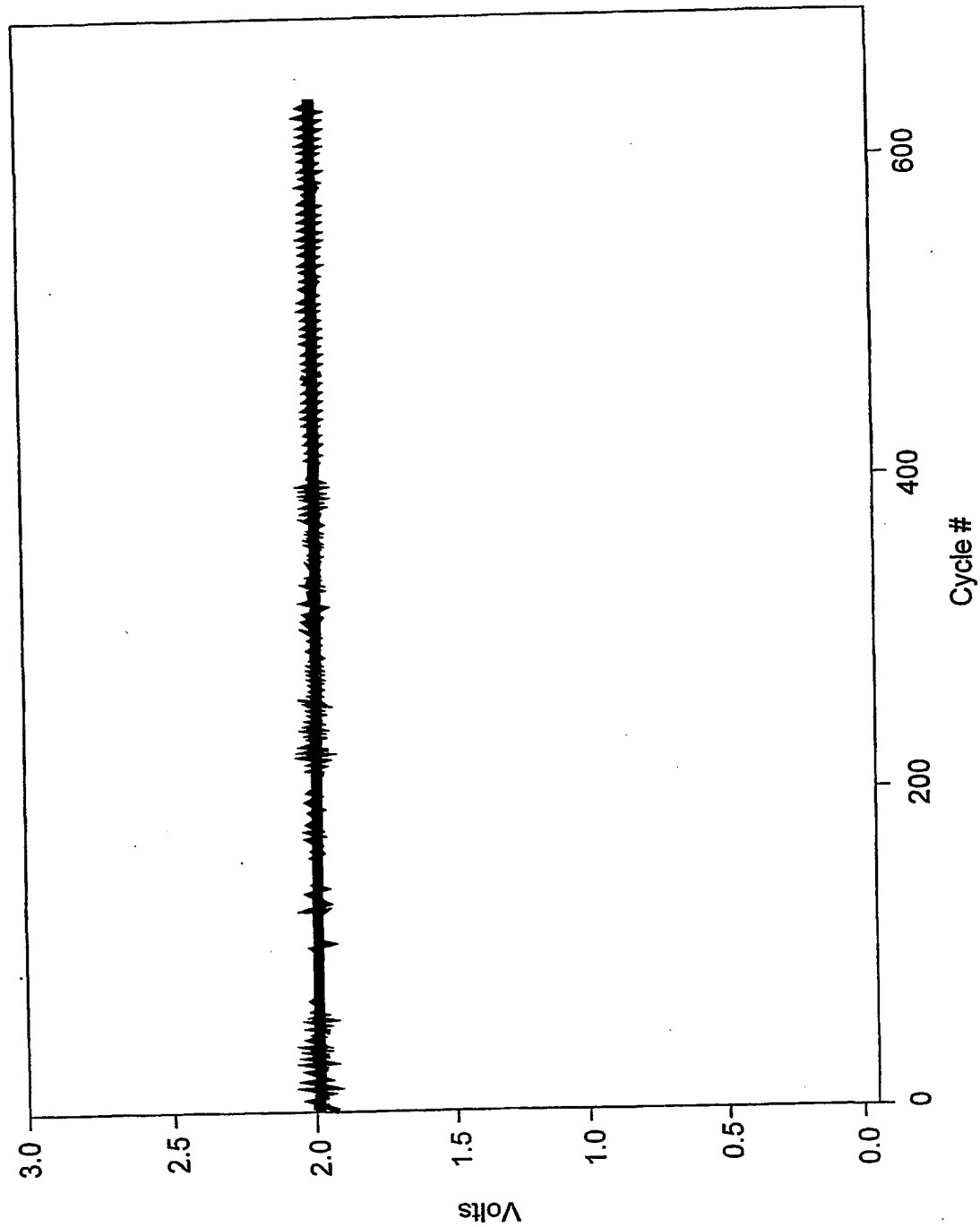
FIG. 5

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Example	maximum % utilization	% utilization during cycling	Number of Cycles	discharge rate mA/cm ²
1	11%	11%	600+	~0.1
2	~55%	~40%	70+	~0.1
3	~50%	~40%	70+	0.5
4	65%	~60%	35+	~0.1
5	~35%	~30%	30+	1.0
6	50%	~40%	50+	0.5

FIG. 6

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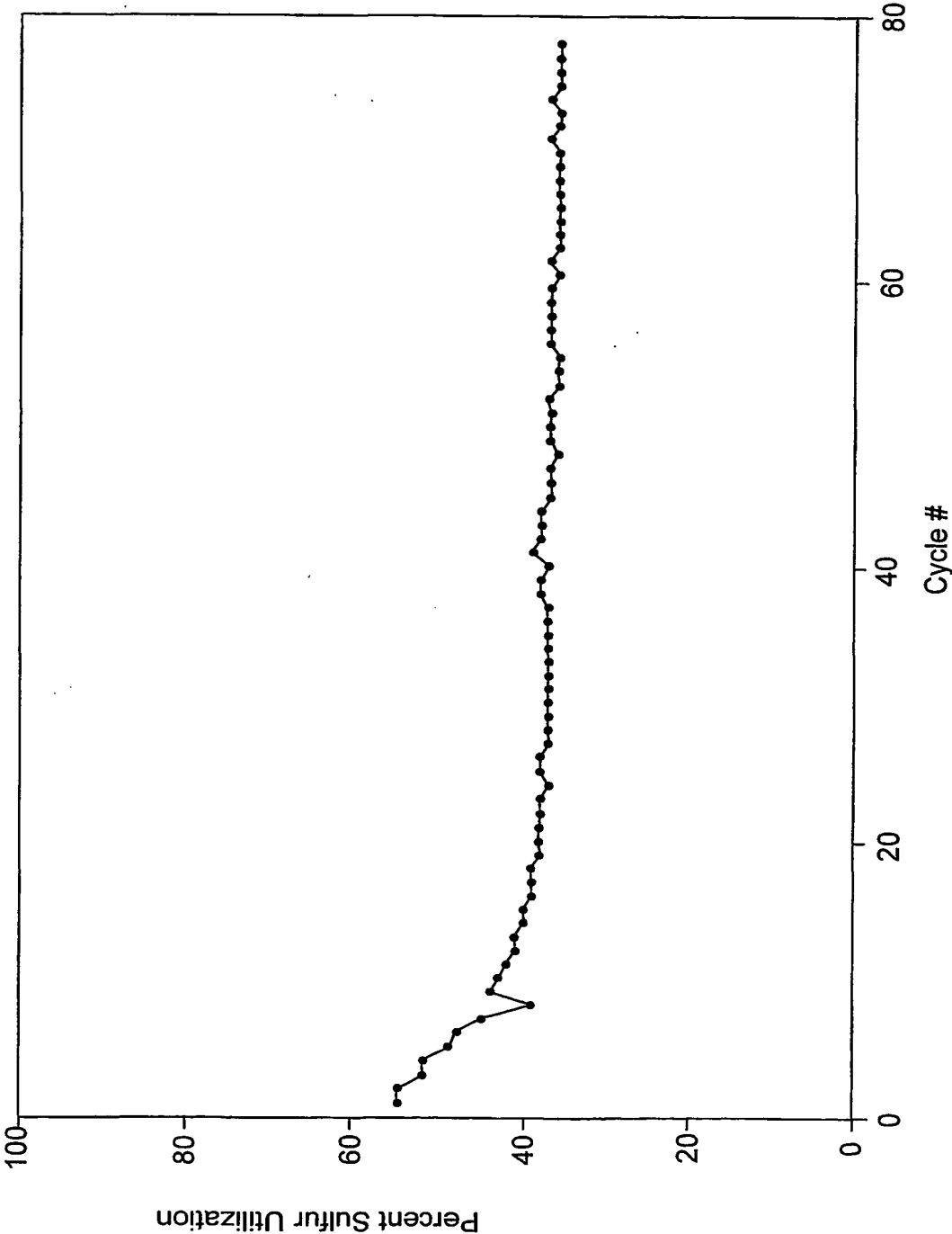


End of discharge voltage vs number of recharge cycles (11% Sulfur Utilization, 25 °C)

FIG. 7

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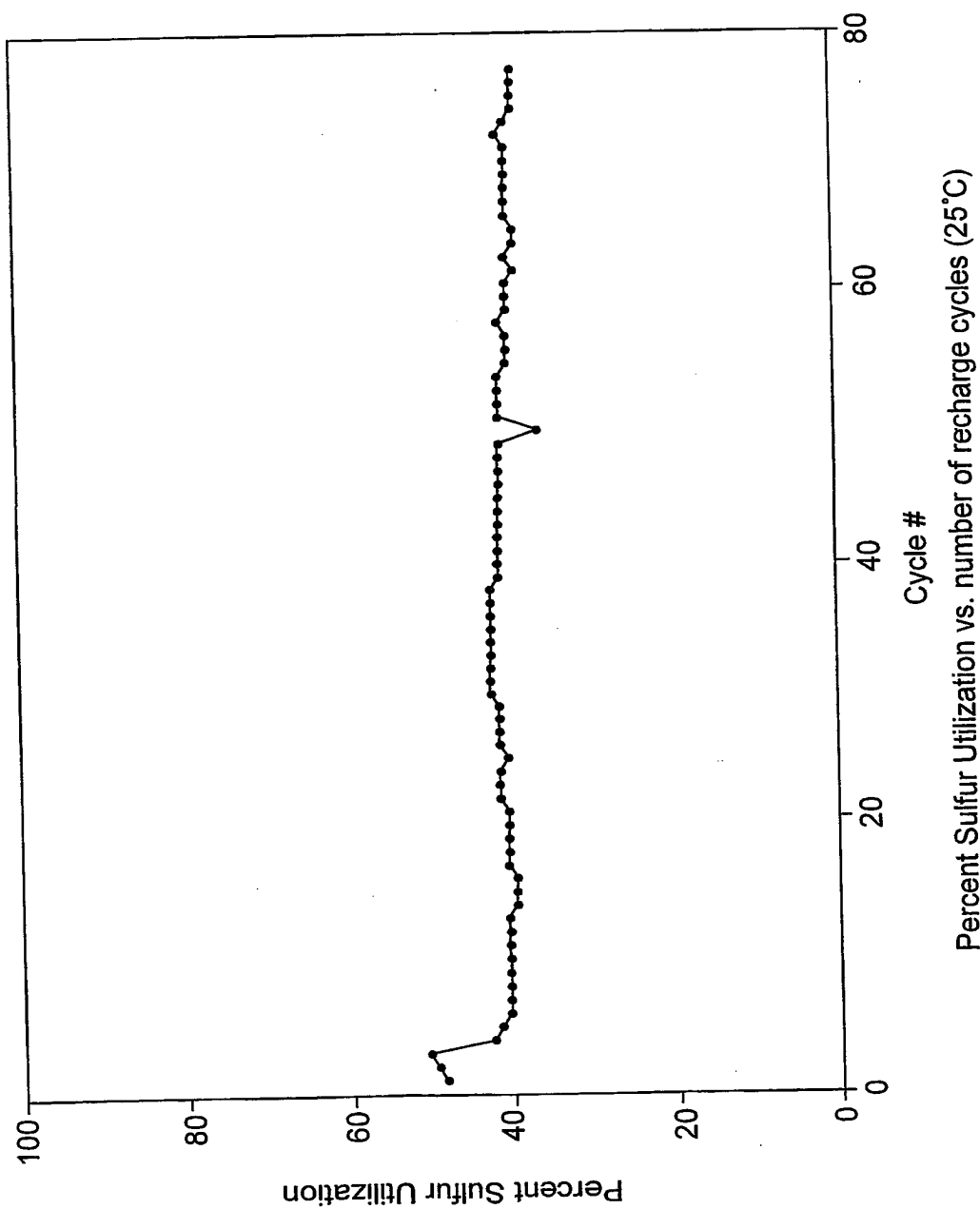
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Percent Sulfur Utilization vs. number of recharge cycles (25°C)

FIG. 8

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**FIG. 9**

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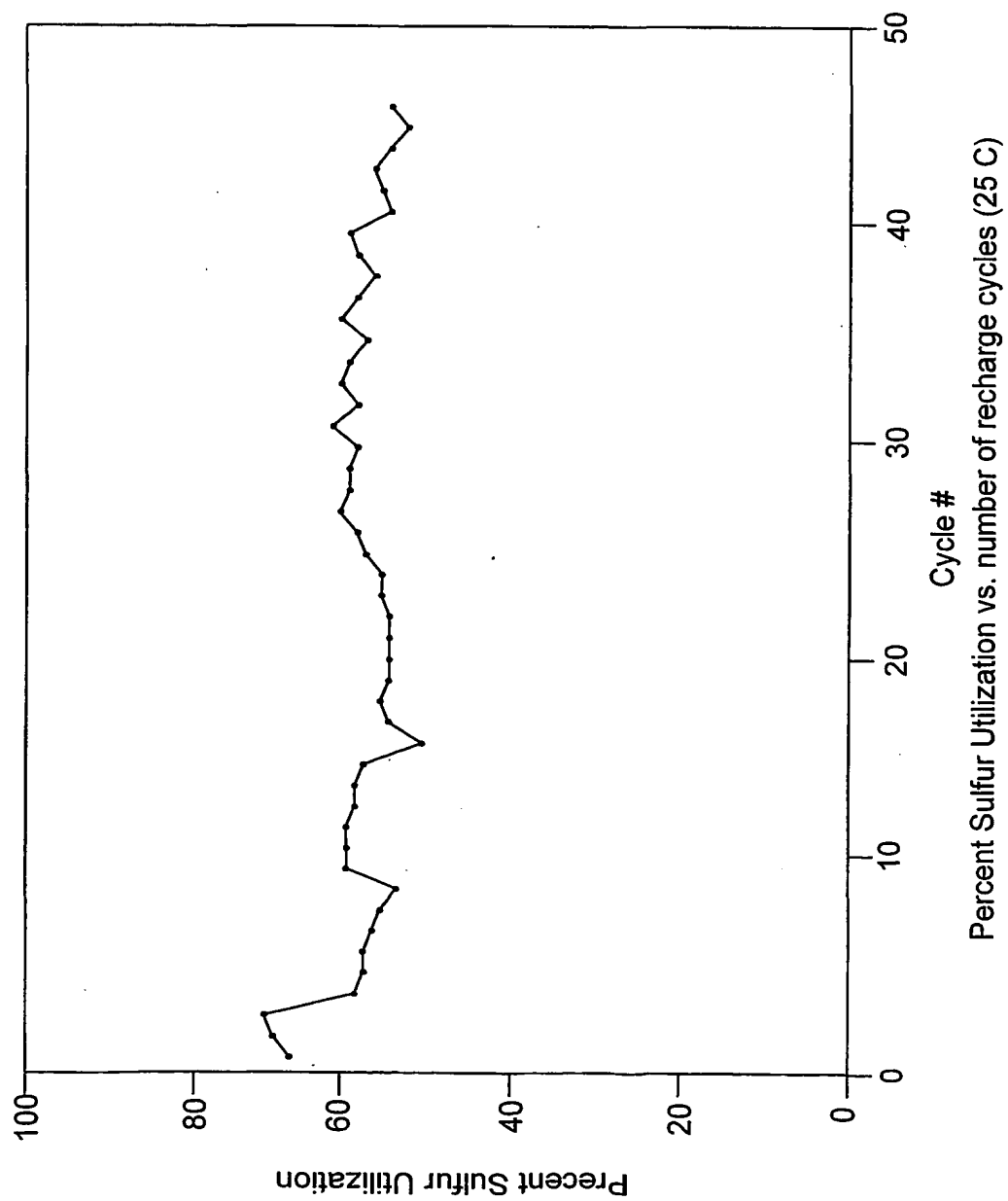
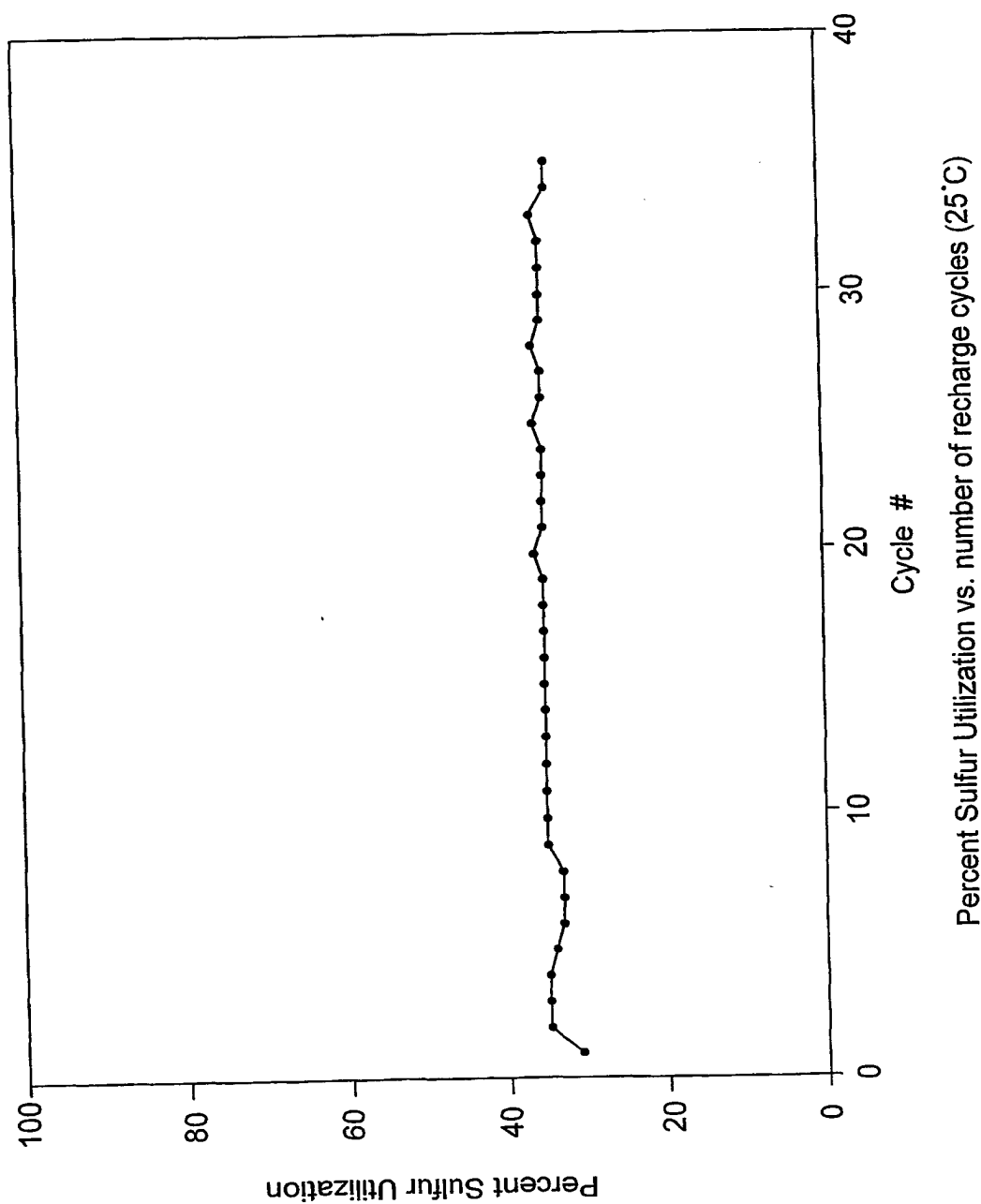


FIG. 10

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**FIG. 11**

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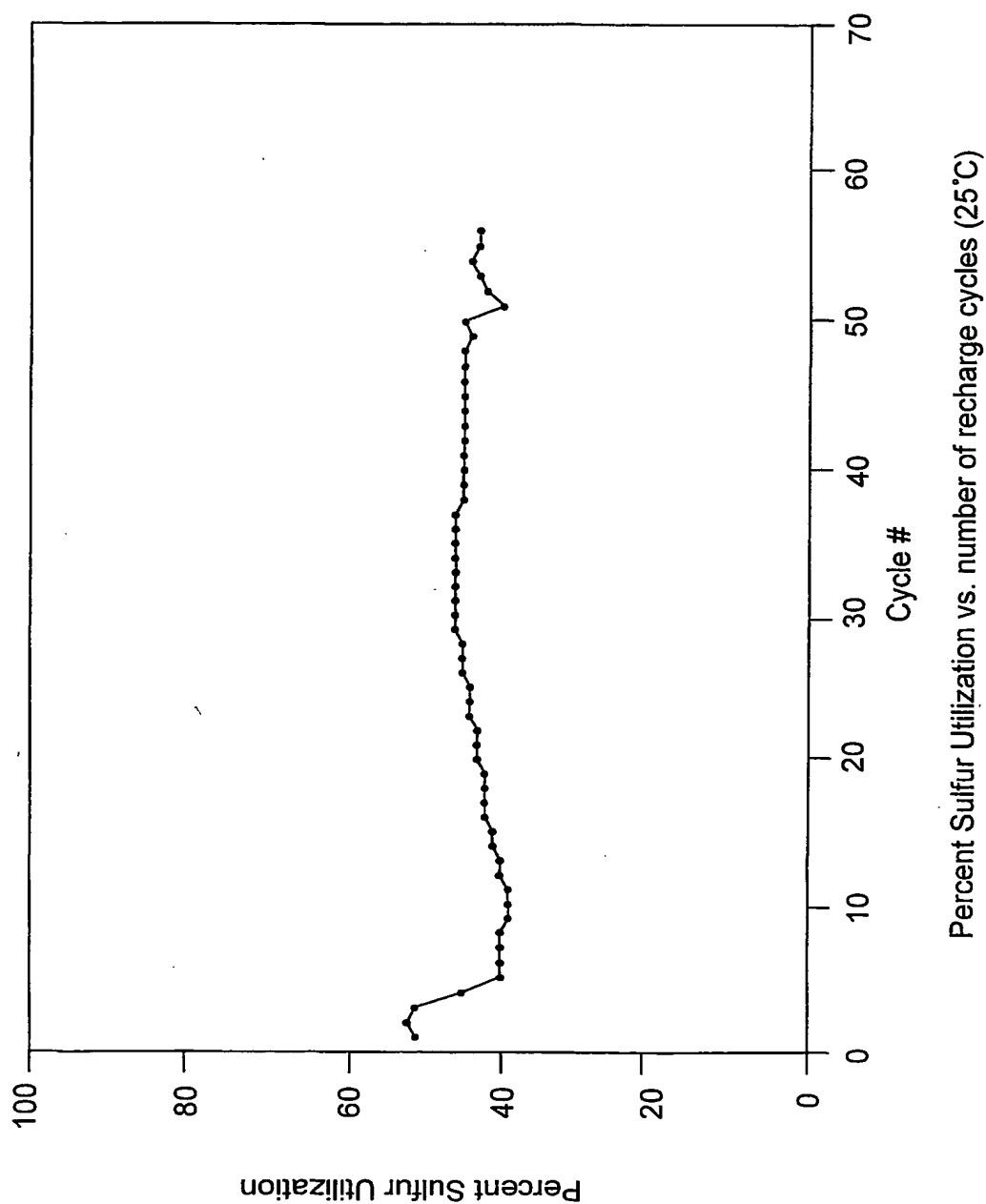


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/02909

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01M 4/58, 6/16

US CL :429/105

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/105, 325, 328, 329, 338, 339

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST (Derwent)

search terms: sulfide, sulphide, solvent, dissolve\$, cathod\$, catholyte

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,806,369 A (DEY et al) 23 April 1974, col. 3, lines 13-23, col. 4, lines 55-56.	18-25
Y		26
Y	US 4,237,200 A (WEDDIGEN) 02 December 1980, col. 1, lines 10-14, col. 2, lines 25-29.	26
A	US 4,469,671 A (BENNETT et al) 04 September 1984, col. 5, lines 1-10.	1-27
A	US 4,917,974 A (DE JONGHE et al) 17 April 1990, col. 3, lines 43-68.	1-27
A	US 5,506,072 A (GRIFFIN et al) 09 April 1996, col. 2, lines 47-67.	1-27

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

12 APRIL 2001

Date of mailing of the international search report

06 JUN 2001

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